















## THE

36

# AMERICAN JOURNAL OF SCIENCE.

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## AMERICAN JOURNAL OF SCIENCE

## [FOURTH SERIES.]

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## ART. I.— The Thermodynamic Relations of Hydrated Glass ;\* by C. BARUS.

1. FURTHER treatment of the fusible water-glass described in the preceding communication + has brought out the following points: During the first or opaque stage of the reaction of hot water on glass (200°), volume-contraction  $(\frac{v}{V})$  and increase

of compressibility  $(\beta)$  are both marked phenomena. During the second stage the water-glass becomes more and more clear and limpid. Volume-contraction falls off asymptotically to zero. Compressibility, after passing through a pronounced maximum which may be even larger than 500/10° per atmosphere, diminishes with great rapidity to the probable isothermal value for pure water (about 100/10°). The relation of change of compressibility to the corresponding volume-contraction (per unit of volume, cold), i. e.  $\delta \beta/(\delta v/v_0)$ , remains throughout of nearly the same order, lying within an interval of  $10/10^{\circ}$  to  $20/10^{\circ}$ , and nearer the former limit so far as measurable. The total apparent volume-contraction of the hot column of water-glass may reach 30 per cent.

2. On cooling *bubbles* appear in the clear water-glass in great number, showing it to contract on solidifying from the center outward (centrifugally), like a Prince Rupert drop. The solid water-glass is in appearance as hard and brittle as ordinary glass,

\*Read before the Nat. Academy of Sciences, Nov. 16th, 1898. †This Journal (4), vi, p. 270, 1898; cf. this Journal (3), xli, p. 110, 1891. The experiments of this paper ending with compressibilities as high as 200/10<sup>6</sup>, relate chiefly to the opaque stage.

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from which it differs in refraction and density. Capillary tubes at the end of the process have become glass rods. The original thread of water is replaced by a solid core of waterglass more than twice the original diameter.\*

Nevertheless all capillary tubes with a solid core of this kind *break* throughout their length in the lapse of time, however carefully cooled. Cf.  $\S$  5.

3. An explanation of these phenomena may be given in the terms of the compressibility observed along the successive isotherms for the different concentrations of glass solution at 210°. This at first shows a relatively small value, implying a steep isotherm in a Clapeyron (pv) diagram. Thereafter compressibility passes through a relatively enormous value (over 5 times the initial result), implying a nearly horizontal isotherm. The reaction ends with even smaller compressibility than the first observed, implying steeper isotherms than the initial curves. Now although these isotherms are all at the same absolute temperature, the water-glass is becoming continually more concentrated and viscous. Hence the corresponding temperatures of the isotherms in van der Waals' sense are continually decreasing. It follows that the reaction considered as a thermodynamic process is a march through the *critical region* of certain phases of the water-glass examined.

4. In the light given by J. W. Gibbs's famous investigations, one may arrive at clear notions by adopting but two phases of the water-glass, for comparison. Many phases may coexist; two are selected in the interest of brevity and called phase 1 and 2, respectively. During the earlier stages of the reaction (dilute water-glass) phase 1 is stable. At the end of the reaction (concentrated water-glass, subsidence of volume contraction) phase 2 is stable. Both cases correspond to steep isotherms. Toward the middle region of the reaction (maxima of compressibility) phases 1 and 2 are mutually stable in presence of each other. Hence the horizontal isotherms corresponding to the critical region are cut through in a march from greater to smaller corresponding temperatures.

That phase 2 is really unstable during the first stage of reaction is shown by the approximate constancy of the values of compressibility, throughout intervals of pressure as high as could be applied. For instance, at 185°,

Interval, $p =$	20-100	100-200	200-300	300 - 400	atm.
$10^6 \times \beta =$	146	144	142	146	

## And fifteen minutes later

$10^{6} \times \beta = 188$ 17	6 201	189.
--------------------------------	-------	------

\*Diameters of threads of water and of water-glass respectively in tube No. 4,  $\cdot024$  and  $\cdot071^{cm};$  in tube No. 5,  $\cdot033$  and  $\cdot059^{cm};$  in tube No. 6,  $\cdot053$  and  $\cdot125^{cm};$  etc.

Again, during the intermediate stage, water-glass is non-resilient: yielding remarkably to increase of pressure, it refuses to expand when pressure is removed. The last stage is again elastic but relatively incompressible.

The extreme compressibility of water-glass during the stated intermediate stage deserves especial comment. Beginning with igneous glass and water<sup>\*</sup> with compressibilities of the order of  $3/10^{\circ}$  and  $100/10^{\circ}$  respectively at  $210^{\circ}$ , values are reached in water-glass which exceed  $500/10^{\circ}$ . One may even compare this result with so volatile a body as ether at different temperatures and between 100 and 200 atm., as follows:

Temperature $=$	$29^{\circ}$	65°	100°	$185^{\circ}$
$\beta \times 10^{\circ} =$	156	207	305	741

Yet the water-glass solidifies in the cold to a hard colorless body quite resembling igneous glass.

5. Made in quantities in a large digester, water-glass is obtained as a nearly homogeneous compact body, adhering forcibly to the walls of the retort, from which it must be removed with wedge and hammer. A small lump held above a caudle flame soon fuses with loss of water to a milk-white pumice. Left without interference in the cold for several weeks or months, it spontaneously cracks and crumbles, eventually becoming a loose mass breakable in the fingers, while the original lump could be broken only with a hammer. In the cold, therefore, phase 2 is unstable and passes back spontaneously into phase 1. Water is set free, probably under great pressure, and hence the gradual crumbling of the mass. When compared with the disintegration of minerals, we have here an example of an enormously rapid chemical reaction, in solids. The breakage of capillary tubes in the lapse of time instanced above, § 2, is thus explained.

\*The rapidity with which water attacks glass vessels at 210° makes it impossible to obtain more than an estimate of its compressibility. See my earlier paper.

Brown University, Providence, R. I.

## ART. II.—Platinum and Iridium in Meteoric Iron; by JOHN M. DAVISON.

[Read before the Rochester Academy of Science on October 11, 1898.]

Some time ago a color reaction, given by potassium iodide with a residue from a solution of Coahuila meteoric iron, led me to suspect the presence of platinum. To test the matter, three attempts were made to separate this element from meteoric iron; the first with 108.6 grams of the Coahuila iron; the second with 500 grams of the same iron; the third with 464 grams of the Toluca iron. The hydrochloric acid solution of these irons left a fine black sediment consisting mainly of minute, tetragonal, prisms of rhabdite; minute, black, irregular crystals, which may also be rhabdite; carbon, and a little stony matter.

From this sediment platinum was obtained in each analysis. There was got from the 608.6 gms. of Coahuila iron 0.014 gms. of metallic platinum, and 0.0015 gms. of a black powder, insoluble in nitro-hydrochloric acid, but, after fusion with zinc, dissolving in that acid and giving with ammonium chloride a dark-red crystalline precipitate, which is probably ammonium iridi-chloride.

From the 464 gms. of Toluca iron a few crystals of potassium platinichloride were obtained. These show a reddish color, and probably contain iridium. The hydrochloric acid treatment of 500 gms. of Coahuila iron left 9.386 gms. of residue: that of the 464 gms. of Toluca iron left 0.944 gms. of residue, which contained more stony matter than did that from the Coahuila. This stony matter was much decomposed by the acid.

Careful search was made for microscopic diamonds. None were found in either meteorite. The few transparent grains, left with the carbon after all soluble matter had been removed, were decomposed by hydrofluoric acid.

From these analyses all platinum utensils were, of course, carefully excluded, the reagents tested, and all precautions taken against accidental contamination.

ART. III.—Studies in the Cyperaceæ; by THEO. HOLM. VIII. On the anatomy of some North American species of Scleria. With figures in the text, drawn by author.

HAVING discussed the composition of the inflorescence in a previous article,\* let us pass to examine the anatomical structure of some of our native species: S. pauciflora Muhl., S. triglomerata Michx., S. oligantha Michx., S. Baldwini Steud., S. ciliata Michx., S. filiformis Swtz., S. Elliottii Chapm., S. Torreyana Walp., S. reticularis Michx., S. hirtella Swtz. and S. verticillata Muhl.

### The root.

All our species are perennial and the roots are generally very strong and develop especially from the lower side of the rhizome; they possess much the same structure as has been described before as characteristic of roots of other genera of this large order, but differ from these, however, by the development of the innermost three or four layers of the bark-parenchyma into a sheath of very thick-walled cells, which surrounds the endodermis. This sheath, in connection with the very thick-walled endodermis, forms a very strong mechanical support to the central-cylinder. Otherwise the root shows an epidermis of usual structure, a hypoderm and an outer bark with large lacunes from the tangential collapsing of the cells, in contrast to the inner layers (B

in fig. 1), which, as described above, forms a very solid tissue.

The endodermis represents a typical O-endodermis, and surrounds a pericambium of normal structure. There are several large vessels in alternation with groups of leptome, and the innermost part of the central cylinder is occupied by a large mass of thickwalled conjunctive tissue.

This structure of the root was observed in species from various



FIG. 1. Root of *S. pauciflora*; transverse section. B, inner bark; End., endodermis; P, pericambium. × 400.

localities; from low, swampy ground and from dry, sandy soil in High Pine woods of subtropical Florida.

\* This Journal, vol. v, January, 1898, p. 47.

## The rhizome.

While the ramification of the stem underground is sympodial in our species, we may, nevertheless, distinguish three forms or modes of growth, viz: cespitose, creeping and tuberous. The first of these is exhibited by S. verticillata, and partly, also, by S. reticularis and S. Torreyana, and does not differ from the usual cespitose rhizomes of other Cyperaceæ. S. ciliata and S. hirtella have creeping rhizomes reminding one of *Fuirena scirpoidea*, which we have described in a previous paper.\* The third form, the tuberous, is well exemplified by S. pauciflora and partly, also, by S. filiformis and S. Elliottii. In these species we notice that the rhizome is very much branched with relatively short internodes, densely covered by rudimentary sheathing leaves. The two basal internodes of each flower-bearing shoot are, furthermore, distinctly swollen so as to give the whole rhizome a peculiar knotted appearance. It is the basal internodes of the axis of first order that show such swelling, while the secondary axis grows out as a short, creeping and rather slender branch.

The development of these forms of rhizomes does not seem to depend upon the character of the soil, since the creeping is noticed in damp (S. hirtella) as well as in very dry sandy soil (S. ciliata). The cespitose form is especially characteristic of S. verticillata, which was collected in damp soil, like S. reticularis and S. Torreyana. The third form is common to species from dry, sandy to rich or swampy ground. Examining the internal structure of the rhizome of S. pauciflora, we notice a thick-walled hypoderm of about three layers inside the epidermis, and bordering on a large bark-parenchyma of thinwalled cells, which contain deposits of starch. The endodermis is not very well differentiated, but seems to consist of rather irregular, thick-walled cells. The innermost part of the rhizome consists of a large, starch-bearing fundamental tissue in which a number of collateral and perihadromatic mestomebundles are imbedded, each of which is surrounded by layers of stereome. A corresponding structure is, also, noticeable in the tuberous base of the stems, but in these we observed a distinct and thin-walled endodermis, and noticed that the stereome around the mestome-bundles is only weakly developed.

In *S. ciliata* and *S. hirtella* we find a similar structure, but the cells of endodermis are more thin-walled. The stereome when compared with that of *S. pauciflora* is much heavier in *S. hirtella*, and much weaker in *S. ciliata*. Reservoirs of tannin were observed in all three species, and seemed to be especially abundant in the bark and fundamental tissue of *S. ciliata*.

\* This Journal, vol. iv, July, 1897, p. 25.

## The aerial stem

which bears the inflorescence is sharply triangular in our species, glabrous or sometimes covered with a few, unicellular hairs along the upper part of the edges, and these are sharply pointed and directed upwards. As in most of the other *Cyperaceee* with sympodial shoots, the flower-bearing stem is in *Seleria* preceded by a few leaves, which winter over.

In its anatomical structure the stem of S. pauciflora shows a distinct cuticle and an epidermis with very thick outer walls. The characteristic siliceous cones which we have mentioned in our previous papers are, also, noticeable in this genus, in those cells of epidermis which lie over the stereome. The barkparenchyma contains chlorophyll and consists of a compact tissue with several tannin-reservoirs scattered here and there. It is interrupted by the stereome, which covers the leptomeside of the mestome-bundles, reaching through the bark outwards to the epidermis. Viewed in transverse section, the stereome is seen to form a large group between the sides of each of the three angles of the stem, while the angle itself is occupied by bark-parenchyma. The mestome-bundles are arranged in two alternating bands, the outer consisting of large and small ones, the inner only of large ones completely imbedded in the pith, which is solid in this species. A like structure occurs in the lateral peduncles, which, however, are covered by hairs of the same shape which we have described as characteristic of the main stem.

The structure of the angle of the main stem seems to offer very good anatomical characters for the species of Scleria, and the following differences have been noticed. In S. pauciflora the angle is occupied by bark-parenchyma, which partly surrounds a very small mestome-bundle with little or no support of mechanical tissue on its leptome-side. Inside of the bark follow, then, heavy layers of stereome, which form a solid bridge between the two sides of the angle, and which support a very large mestome-bundle. This same structure is, also, characteristic of S. triglomerata, S. oligantha, S. Baldwini and S. Elliottii. In S. reticularis, S. Torreyana and S. ciliata, on the other hand, the angle itself is occupied by a small group of stereome which borders inwardly on some strata of bark parenchyma in which a very small mestome-bundle is situated. Next to that occurs a large mass of stereome which connects the two sides of the angle as in S. pauciflora, and which supports a mestome-bundle with a hadrome of considerable development. S. verticillata, S. hirtella and S. filiformis illustrate a third form of structure, since the angle contains here a single, large mestome-bundle, supported by a strongly developed stereome on the leptome-side.

Some other divergencies may be observed in the relative development of the bark-parenchyma and the stereome of the stem; we notice, for instance, a very thin bark-parenchyma in *S. oligantha*, in contrast to *S. filiformis* and *S. ciliata*, where the same tissue forms strata of rather large dimensions. The stereome seems to be present in larger groups and to be more thick-walled in *S. pauciflora*, *S. Baldwini* and *S. ciliata* than in any of the other species. The pith is broken by lacunes in *S. Torreyana*, *S. reticularis* and *S. filiformis*, but is solid in the other species.

## The leaf.

The leaves of our species are provided with a tubular sheath and a long linear blade, which is very narrow in the North American species with the exception of *S. triglomerata. Scleria* is marked by the total absence of a ligula. Projections from the epidermis, such as spines or warts, are scarce, and *S. triglomerata* seems to be the only one of our species in which continuous rows of rather sharp and curved projections are visible above the stronger ribs in the leaf-blade. Hairs are, on the other hand, common, and occur as a more or less dense pubescence upon the sheaths of all our species, or as scattered, soft hairs along the margins of the leaf-blade, besides and not infrequently upon the upper face of the blade, covering the furrows between the stronger ribs.

The anatomical structure of the leaf-blade seems to be very uniform in our species, yet exhibits some peculiarities which enable us to separate the species, at least in groups by anatomical characters. In *Scleria pauciflora* the stomata are confined to the lower face of the leaf-blade, forming longitudinal rows underneath the mesophyll. The cells of epidermis are rather



FIG. 2. Leaf of S. pauciflora; transverse section; BC, the bulliform cells.  $\times\,120.$ 

large and thin-walled on both faces of the blade, and form a single group of the characteristic bulliform cells above the midrib (B C in fig. 2). The other cells of epidermis of the upper face are remarkably large, but without attaining the shape or arrangement of proper bulliform cells. The mesophyll forms throughout a compact tissue, containing much chlorophyll and is differentiated as a palissade tissue on the upper face of the blade. Tannin-reservoirs are not uncommon in the mesophyll. Mestome-bundles of two degrees of development separate the mesophyll, which shows a distinct constriction at each bundle, as shown in the accompanying figure 2. A usual colorless parenchyma-sheath and a rather thin-walled mestome-sheath surround the bundles, the larger of which are supported by stereome on both faces, above and below. The smaller mestome-bundles show only a few stereome-cells on their leptome-side.

The same distribution of bulliform cells as representing only one group above the midrib is also met with in other species of Scleria, and appears to be the commonest arrangement. We have observed it in S. triglomerata, S. oligantha, S. ciliata, S. filiformis, S. Elliottii, S. Baldwini and S. reticularis. But in none of these species does the leaf-blade show the deep furrows which we observed in S. pauciflora, and which gives the section the peculiar constricted appearance. The epidermiscells of the upper face are, however, also very large in these species, increasing in size towards one of the largest of the lateral ribs, but without becoming specialized as proper bulliform cells. It is, furthermore, characteristic of these species that one or two of the lateral ribs project very strongly on the upper face, while in S. pauciflora they were all situated below the surface, in shallow furrows. Stomata occur on both faces of the blade in these species, in contrast to S. pauciflora. Some, but slight, variations were also noticed in the thickness of the cell-walls of epidermis and stereome; we observed, for instance, a very thick-walled epidermis in S. ciliata, S. Baldwini, S. filiformis, and S. Elliottii; a thick-walled stereome in S. ciliata and S. Baldwini, besides that the mestome-sheath showed a more prominent thickening in these two species than in any of the others. S. reticularis is the only species in which the stereome on the upper face of the leaf-blade is separated by mesophyll from the mestome bundles. Characteristic of the remaining three species: S. Torreyana, S. hirtella and S. verticillata is the presence of more than one group of bulliform cells, there being three between the larger lateral ribs in S. Torreyana besides the one above the midrib. In the two other species the epidermis between each two mestome-bundles and above the midrib is developed as bulliform cells, the number of groups corresponding to the width of the leaves, about four on each side of the keel of S. verticillata, eight or nine in S. hirtella. The other tissues, the mesophyll, with reservoirs of tannin, the stereome and the mestome-bundles show much the same

structure as described above for *S. pauciflora*, as regards their development and distribution.



FIG. 3. Leaf of S. verticillata; transverse section; BC, bulliform cells. × 120.

Scleria verticillata and S. hirtella differ, however, from the other species of Scleria, which we have examined, and as a matter of fact from all the other Cyperaceæ which we have studied anatomically, by possessing some very peculiar incrustations of silica upon the radial walls of the bulliform cells. The accompanying figure 4 illustrates two bulliform cells in



FIG. 4. Two bulliform cells from the leaf of S. verticillata with incrustations; transverse section.  $\times 320$ .

FIG. 5. A macerated bulliform cell of S. verticillata with incrustations.  $\times$  320. FIG. 6. Incrustations from bulliform cells of S. verticillata,  $\times$  320.

transverse section, with incrustations upon the radial-walls, the outline of which are indicated by dotted lines in our figure. These incrustations form granular masses of a whitish color and are present in almost all the bulliform cells, but varying somewhat in shape and size. By burning sections of the leaf to white ashes and then adding a few drops of hydrochloric acid these incrustations become very conspicuous and assume a clear brown color like sepia. Figure 5 illustrates a macerated bulliform cell, and we notice here that the incrustation has taken place to the same extent on both of the adjoining radial cell-walls. A part of the radial cell-wall upon which the incrustation takes place contains also silica and remains as fragments attached to the incrustations after they have been macerated, which is to be seen in the accompanying figure 6. Figs. a, b and c show the incrustations as seen from within the cell with a part of the cell-wall still remaining; figure d represents one of the smallest incrustations, seen from above. These silicious incrustations dissolved in a concentrated aqueous solution of potassium in about forty-eight hours.

Silicious incrustations are also known to occur in the *Gramineæ*, and Dr. Aug. Grob has lately published a very important treatise of this subject.\* He has, however, confined himself to the *Gramineæ*, and judging from his descriptions and figures, the incrustations which we have observed in *Scleria* differ very much from any of those that have been found in the *Gramineæ* or other monocotyledonous orders.

The pericarp of *Scleria* contains also a vast amount of silica. It lies in two distinct strata of which the outer one is built up by a homogeneous tissue of polyëdric cells; the inner part consists of a single layer of cells with very long and thin radial walls. It is the outer tissue that undergoes the incrustation, and when macerated the silicified cells form some very beautiful structures like stars, for instance, in *S. pauciflora* and others. Considered from an anatomical point of view, the North American species of *Scleria* show several characters in common; thus it does not seem probable to distinguish all the species by means of their structure alone. We have, nevertheless, enumerated the most salient points in the accompanying table, from which the anatomical characters may be readily seen, at least in some of our species.

		EAF.		_		_		OIL.	м. 			
	Bulliform cells ouly above midrib.	Bulliform cells above midrib and three lateral groups.	Bulliform cells above mid- rib and four groups on each side.	Bulliform cells above midrib and eight or nine groups on each side.	Bulliform cells with incrus- tations.	Stereome separated from mestome-bundles by meso- phyll.	Angle occupied by bark- parenchyma.	Angle occupied by stereome and two mestome-bundles.	Angle occupied by stereome and one mestome-bundle.	Pith solid.	Pith with lacunes.	And the second
S. pauciflora S. triglomerata S. oligantha S. Baldwini S. Giliata. S. filiformis S. Elliottii S. Torreyana S. reticularis S. hirtella S. verticillata	++++++ +			+	++		++++	+     + +	+     + +	+++++ + + + + + + + + + + + + + + + + +		

\* Grob, August, Beiträge zur Anatomie der Gramineen-blätter, Bibliotheca Botanica, Stuttgart, 1896, p. 34. Although the first four of these species are not to be separated by the anatomical characters, which we have pointed out, they are nevertheless readily distinguished by their morphological; the other species seem on the other hand to be equally well distinguishable by anatomical and morphological divergences.

In considering the character of soil and climatological conditions of the localities from where our material has been brought together, one might feel inclined to designate these plants as belonging to xero- or hydro-philous societies. Their structural peculiarities, however, do not point towards any distinction of that kind. Scleria pauciflora, for instance, from wet ground in the vicinity of Washington, D. C., does not differ in any very marked degree from S. triglomerata, which we collected in dry sandy soil in subtropical Florida; furthermore S. ciliata, an inhabitant of the High Pine-woods of Florida, shows no strictly xerophytic characters when compared with S. reticularis, a bog plant. While certain species, as S. reticularis, S. filiformis and S. Torreyana, collected in a rather wet ground, possess a stem with a more or less broken pith, other species from similarly damp localities have perfectly solid stems. It seems as if the North American species of Scleria are very little susceptible to variation due to changes in environment and that they are not to be placed into any special society, either among the "xero- or hydro-phytes."

Brookland, D. C., August, 1898.

## ART. IV.—Concerning Regnault's Calorie and Our Knowl-edge of the Specific Volumes of Steam; by G. P. STARK-WEATHER.

THE volumes of saturated steam at various pressures customarily used are those determined from the latent heats. Since the latter depend almost entirely upon Regnault's experiments, the question of his 'calorie' is of importance. In calculating the 'heat of the liquid' and 'total heat' Regnault assumed that within the calorimeter range, say from 0° to 30° C., the specific heat of water was sensibly constant. Whether this is so or not depends upon the thermometric scale used. If mercurial it might be so, but if the scale was that of the airthermometer, which is the one to which Regnault usually reduced his observations, it certainly would not.

Bosscha\* in 1874 remarked that in the experiments under consideration there was no record of the calorimeter temperatures being reduced to the air-thermometer, and accordingly made corrections to Regnault's formula for 'heat of the liquid,' although he still assumed that the specific heat of water was constant within the calorimeter range. To this Regnault replied that the calorimeter temperatures were reduced to the air-thermometer, but as this was over twenty years after the experiments were conducted there has always been more or less uncertainty to many minds.

The writer hopes to present some evidence from Regnault's experiments themselves corroborating his statement, and will construct formulæ taking into account the variation of the specific heat of water from 0° to 30°. The agreement between Rowland and Griffithst regarding this variation is so exact, and their methods were so accurate, that between the limits mentioned it can be regarded as determined. Their results are expressed according to the Paris nitrogen scale, but the specific heats according to Regnault's air-thermometer would not differ qualitatively from them, and ought not to differ much quantitatively. The only person, so far as the writer is aware, who has looked at the subject in the light of recent experiments is Ekholm,<sup>‡</sup> but he concludes (it seems to the writer incorrectly) that Regnault's calorimeter temperatures were not reduced to the air-thermometer, and accordingly makes no corrections for the variation in the specific heat at low temperatures, supposing it to be constant according to the mercurial thermometer.

\* Ann. Phys. und Chem., Jubelband, p. 549.

† Phil. Mag., xl, p. 449, 1895, and Proc. Roy. Soc., lxi, p. 479, 1897. ‡ Bihang till Handlingar Svensk. Vet. Akad., xv, 1889, No. 6, p. 27.

Before making use of Regnault's experiments on heat of the liquid it is well to note the error discovered by Velten\* in them. In Regnault's table the second column gives the weight of cold water in the calorimeter, P; the third, the weight of hot water,  $p_j$  the seventh, the temperature, T, of the hot water according to the air-thermometer; the eighth, the initial temperature of the calorimeter,  $t_0$ ; the ninth, the final temperature of the calorimeter,  $t_1$ ; the eleventh ( $t_1-t_0$ ) corrected; the last, the mean specific heat between  $t_1$  and T, x. Then we should have, according to Regnault's assumption that at low temperatures the specific heat is practically constant.

$$x = \frac{\mathbf{P}(t_1 - t_0)}{\mathbf{P}(\mathbf{T} - t_1)}.$$

Now Velten has found that out of Regnault's forty experiments in only five does his value of x agree with this formula; in twenty-two cases the difference is insignificant, while in thirteen cases there is complete disagreement. Velten has ascribed this discrepancy to errors in calculation, but it is very strange that erroneously calculated these values of x should bear a good agreement with the others and as 'correctly' calculated by Velten should not. Sutherland+ has almost conclusively shown that the error is one in the copying of Regnault's numbers into the tables, namely, that Regnault in these thirteen experiments, which belong to a different series from the others, copied a wrong set of numbers for the weight of hot water, and that his values of x are the correct ones. Sutherland's proof is based on considerations of the cubic capacity of the calorimeter, as these very experiments show an unusually large amount of hot water. In fact, as the numbers stand, there is indicated a total weight of hot and cold water greater than the capacity of the calorimeter.

The writer has made corrections to Regnault's experiments on the heat of the liquid necessitated by the variation of the specific heat within the calorimeter range, but has found that Ekholm's formula fits as well as any. Although this was formed without the above mentioned corrections, nevertheless the latter are considerably smaller than the variations in the experiments themselves. Also in developing the formula Ekholm left out certain experiments which are those the corrections affect the most. The formula is

 $h = t + 0.00000929 t^2 + 0.000000265 t^3,$ 

and is to hold only above 100°.

The unit here is the specific heat at 15° according to Reg-

\* Wied. Ann., xxi, p. 45, 1884. † Phil. Mag., xxvi, p. 302, 1888. nault's thermometric scale, which will be denoted as Regnault's calorie. The formula may be incorrect towards 200° by about 0.3 per cent, but is quite accurate at  $100^\circ$ , since in this vicinity the corrections are very slight whatever be the thermometric scale. It gives for the mean specific heat between 0° and 100° the value 1.00358.

Now if Regnault's scale was that of the air-thermometer, this number should agree with the determinations made by other observers who have used that scale or ones not differing essentially from it. Such determinations have been made by Von Muenchausen,\* Rowland,† Henrichsen,‡ Baumgartner,§ Velten || (two series, one by the method of mixtures, the other with the Bunsen ice-calorimeter), Dieterici, Ludin, \*\* Joly, ++ and Reynolds. 11

Von Muenchausen's work, which was conducted by the method of mixtures, has been criticised by Rowland on the ground that the experiments were performed in an open vessel. An inspection of his tables reveals great discrepancies. Thus as a mean of row I he finds that the mean specific heat from  $26^{\circ}.70$  to  $42^{\circ}.37$  is 1.0033 times that from  $20^{\circ}.07$  to 26°.70. This is impossible, for the specific heat reaches a minimum at 32°, by Rowland's experiments, and there would be necessitated a mean specific heat from 32° to 42° of 1.0033, the specific heat at 15°,  $c_{15}$ , being the unit. This mean specific heat would indicate for  $c_{q}$  the value 1.0102, an increase of 1.4 per cent in ten degrees. Moreover in rows II and III he finds that the mean specific heat from say  $25^{\circ}.7$  to  $42^{\circ}.7$  is 1.0037times that from 17°.3 to 25°.7, an increase over the preceding, whereas according to Rowland's data it should be less. His formula makes  $c_{1-100}$  equal to 1.015  $c_{15}$ .

The writer has made careful comparisons of a similar nature of the experiments of Baumgartner and Velten, and finds even worse discrepancies. Baumgartner makes the mean specific heat from 0° to 100° equal to 1.016  $c_{15}$ , while Velten's two series make it respectively 0.9896 and 0.9929.

The experiments of Henrichsen were performed with the ice-calorimeter. Dieterici, who is an authority on the use of this instrument, has made a careful comparison of them with those of Velten carried out by the same method. He says (reference, p. 443): "The great differences which the experiments made with the ice-calorimeter show, make it probable that this instrument is unsuited for this investigation." More-

11 Nature, June 3, 1897.

<sup>\*</sup> Wied. Ann., i, p. 592, 1877. ‡ Wied. Ann., vii, p. 83, 1879. ¶ Ibid., xr, p. 31, 1884. \* Beiblactter zu Wied. Ann., xx, p. 764, 1896. Proc. Amer. Academy, 1879-80, p. 120.
§ Ibid., viii, p. 648, 1879.
¶ Ibid., xxxiii, p. 417, 1888.

<sup>++</sup> Phil. Trans., clxxxvi A, pp. 322, 323, 1895.

over Henrichsen makes the ratio of the mean specific heat from 0° to 100° to that from 0° to 25° equal to 1.025, a number which is markedly larger than has been obtained by any other investigator.

So far we see that little or no dependence can be placed on the experiments. Rowland's work should be more reliable. His experiments make  $c_{2s-100}$  equal to  $1.0024 c_{1s-2s}$ , or reduced to  $c_{1s}$  as a unit,  $c_{2s-100}$  is  $1.0049 c_{1s}$ , which makes  $c_{0-100}$  equal to  $1.0034 c_{1s}$ . He mentions two other determinations and gives as the mean of all three that  $c_{0-100}$  is equal to  $1.0041 c_{1s}$ .

The very recent work of Ludin was performed with great care. He gives for  $c_{0-100}$  the value 1.00543  $c_{15}$ .

Joly's determination of  $c_{0-100}$  was obtained by the use of his steam-calorimeter, and gives for its value 0.9957  $c_{10}$ . Concerning the accuracy of this instrument we know nothing, and no details are given. He himself says he obtained much larger values in earlier experiments, but he considers this to be more accurate.

We have now left the determinations of Dieterici and These were both by obtaining the mechanical Revnolds. equivalent. Dieterici found by electrical methods (and using the ice calorimeter) that  $c_{0-100}$  was equal to 42.436 megalergs. Griffiths\* has pointed out that he made the error of using the "legal" instead of the "true" ohm, which reduces his value to 42.33. There is also a constant error<sup>+</sup> in experiments made by electrical methods of about one-quarter of one per cent due to the determination of the electrical standard of electromotive force, which reduces this to 42.225. This makes the mean specific heat between 0° and 100° equal to 1.00799  $c_{\rm ec}$ . The experiments of Dieterici were performed with great care, were sixteen in number, and deviated from the mean at most 0.37 per cent, the probable error being 0.05 per cent. But they have one fault, that there is lacking a conclusive determination of the quantity of quicksilver displaced in the ice-calorimeter by a quantity of heat equal to the mean specific heat from 0° to 100°. Bunsen has found it to be 15.41 milligrams, Schueller and Wartha 15.442, and Velten 15.47; Dieterici takes the second value. Velten's values being uncertain, as has been shown, it seems as if less weight should be given to his determination, which would still further reduce Dieterici's value for the mean specific heat from 0° to 100°.

In total opposition to Dieterici stand the recent results of Reynolds. According to him the mechanical equivalent of the mean specific heat from 0° to 100° is 41.83 megalergs, which is

\* Phil. Mag., xl, p. 446, 1895.

<sup>†</sup> Phil. Mag., xl, p. 449, 1895; Proc. Roy. Soc., 1xi, p. 479, 1897, and Johns Hopkins Univ. Circular, No. 135, June, 1898, p. 54. equal to the specific heat at about 20°. His experiments are as concordant as those of Dieterici.

Let us now compare Regnault with these other investigators. The table below gives the fractional deviations of  $c_{0-100}$  according to them from 1.00358  $c_{1x}$ .

(1) Experiments which are unreliable.

Von Muenchausen	(mixtures)	+0.0113
Velten	(mixtures)	-0.0139
Henrichsen	(ice-calorimeter)	+0.0214
Velten	(ice-calorimeter)	-0.0106
Baumgartner	(mixtures)	+0.0124
Joly (	steam-calorimeter)	-0.0023

(2) Experiments in which evidences of unreliability are not present.

Rowland	(mixtures)	+0.0005
Ludin	(mixtures)	+0.0018
Dieterici	(mech. equiv.)	+0.0044
Reynolds	(mech. equiv.)	-0.0020

The first set are grouped so far as possible into pairs of equal probability and nearly balance. Of the second set the last two balance, and the deviations in the first two are very small. As the numbers stand the positive deviations seem to rather outweigh the negative; some additional evidence on the negative side is afforded by the following: Sahulka\* has found for the mechanical equivalent at 58° the value 426·262 kilogrammeters, or 41.81 megalergs, thus making  $c_{ss}$  equal to 0.9981  $c_{1s}$ . Assuming the specific heat to vary linearly with the temperature from 35° to 100°, this would make the mean specific heat from 0° to 100° equal to 0.9992  $e_{1s}$ , the fractional deviation from the value we have assumed being thus -0.00436. This evidence is not entitled to very much weight, however, because Sahulka's experiments deviate from their mean over one-half of one per cent.

It is thus seen that the assumption that Regnault's thermometric scale was that of the air-thermometer makes his value of  $c_{9-100}$  agree well with that obtained by others. It cannot be more than 0.5 per cent out, and is probably much more accurate than that. Any error in it should be ascribed to the unit in which it is expressed rather than to inaccuracies in the experiments themselves.

For temperatures below 100° the writer has formed for his present purposes the following formula :

### $h = 1.00449 t - 0.0001904 t^{2} + 0.000001813 t^{3}.$

#### \* Wied. Ann., xli, p. 748, 1890.

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2

Two of the constants were determined so as to make  $c_{15}$  equal to unity and  $c_{0-100}$  equal to 1.00358, while the remaining constant was adjusted to give a good value to  $c_{so}$ ; the minimum value is reached at 35°. A better agreement might be obtained by the method of least squares, but since  $c_{0-100}$  is not too well known and the remaining data all lie below 40° such nicety would not be justified. Moreover the only use made of the formula is to obtain latent heats from total heats, and also the entropy of dry saturated steam, and the term given by this formula is very small in comparison with the quantities with which it is combined.

The formulæ adopted for the heat of the liquid give us the following for the entropy of water:

l.
Above 100°.
3.015698
1.250174
$\bar{4}.229792$
2490.9

This gives the entropy in kilogrammeters (at Paris) per degree, the zero of entropy being that of water at 0° C. T is the temperature absolute, absolute zero being taken as -273°.7 C.

Regnault's ninth memoir, Memoirs of the Institute of France. vol. xxi, furnishes us with the greater part of our knowledge concerning the total and latent heat of steam. Other experiments have been made by Andrews,\* Favre and Silbermann,+ Berthelot, \$\$ Schall, \$\$ Dieterici, # Hartog and Harker, \$\$ Griffiths, \*\* G. Fuchs, ++ A. Svensson, ++ W. Ramsay and D. Marshall, §§ and Harker. Svensson are at, or in the close vicinity of, 100°. Those by Hartog and Harker and by Harker alone are admitted by the authors themselves to be inaccurate. In all the remainder there is doubt as to what unit the results are expressed in, and they are few in number. Taken at their face value they all give a remarkable confirmation of Regnault's determination at 100°. The following table, taken partly from Griffiths' paper on latent heats, shows this:

\* Chem. Soc. Journal, 1849. ‡ Comptes Rendus, lxxxy, 1877. Wied. Ann., xxxvii, p. 494, 1889. ¶ Proc. Manchester Phil. Soc., 1893-4. \*\* Phil. Trans. clxxxvii, A. 2014, 1869.

\*\* Phil. Trans., clxxxvi A, p. 261, 1895. † Inaug. Dissertation, Erlangen, 1894, and Beiblaetter zu Wied. Ann., xix, p. 559, 1895.

t‡ Beiblaetter zu Wied. Ann., xx, p. 559, 1895. §§ Rep. British Ass., 1895, p. 628. ∭ Mem. and Proc. Manchester Lit, and Phil. Soc. (4), x, p. 38, 1896.
		Number of	Extreme	
Observer.	Temperature.	Experiments.	values of L.	Mean L.
Andrews	100	8	530.8 -543.4	535.9
Favre and Silberman	ın, 99·81	3	532.59-541.77	535.77
Berthelot	100	3	535.2 -537.2	536.2
Schall	100			532.0
Fuchs	100			536.8
Ramsay and Marsha	ll, 100			537.0
Regnault	- 99.88	44	5330 -538.0	536·3

The greatest deviation of these mean values from Regnault's is about eight-tenths of one per cent. To get Regnault's latent heat from his total heat I have used the 'heat of the liquid' from the formulæ already developed.

Consider now Regnault's experiments on total heats. These are divided into four classes, those at or near 100°, those from 119° to 195°, those from 63° to 88°, and last the set from  $-2^{\circ}$ to +16°. He has given as a formula to unite these

## H = 606.5 + 0.305 t.

Take the series at  $100^{\circ}$ , forty-four in number. Neglecting the first six, which Regnault does not regard as so accurate as the others, the mean is 636.67, and the greatest deviation from this is less than three-tenths of one per cent. If we admit the first six the greatest deviation is less than six-tenths of one per cent. When we consider the fact that Regnault purposely varied all his experiments in many ways so far as possible, in order to eliminate constant errors, this close agreement in so many experiments shows that the mean value given above is very exact.

The unit in which this is expressed is determined by the calorimeter range, the average of which was from about  $8^{\circ}3$  to  $20^{\circ}.9$ , from which range the individual experiments did not differ essentially. Accordingly the unit is the specific heat at  $14^{\circ}.6$  according to Regnault's thermometric scale, or practically Regnault's calorie. This we have judged to be the specific heat at  $15^{\circ}$  according to Rowland's scale, and have investigated the possible error in that judgment. There will be accordingly the same possible error in the total heats.

Consider next the experiments above 100°, seventy-three in number. A comparison of the numbers given in Regnault's tables with those given by his formula follows: From 119° to 150° the deviations of the experiments from the formula vary from -0.36 per cent to +0.25 per cent, mostly negative, but are generally very slight. At 153°, or experiment number 32, there is a sudden jump to -0.5 per cent, and a deviation exists varying from -0.2 per cent to -0.65 per cent, averaging -0.5 per cent, and gradually increasing up to 175°.5. Here there is another sudden change, and the deviations vary up to 195° between +0.2 per cent and -0.2 per cent, mostly positive. These sudden changes are rendered much more prominent by the following table. In the first column is given the number of the experiment, in the second the temperature, and in the third the fractional deviation of the observed total heat from that calculated by Regnault's formula.

1	119.25	-·0009	0014	0011	38	155.7	0040	0025	-·0019
2	119 60	0018	0018	-·0015	39	1565	0020	0005	+.0003
3	122.17	0025	0028	0025	40	157.1	-·0046	0031	0024
4	125.2	-·0013	-0003	.0000	41	157.8	0040	0025	0018
5	125.5	0018	0008	0005	42	160.3	0039	0024	0016
6	127.2	0008	+.0002	+.0002	43	160.4	0034	- 0019	0011
7	129.0	-·0011	-·0001	+.0005	44	161.8	0030	0015	-·0007
8	134.4	+.0024	+.0015	+ 0018	45	164.6	<b>—·</b> 0050	0035	-0026
9	134.2	+.0005	0002	0004	46	164.9	0024	0009	·0000
10	135.1	+.0013	+ 0004	+.0001	47	171.6	0020	0035	0024
11	135.0	+.0023	+.0014	+.0012	48	172.6	0059	-0044	0033
12	135.2	0002	0011	0002	.49	172.6	-0059	0044	-·0033
13	135.5	-0013	-·0006	0002	50	172.8	0066	0051	0040
14	135.7	0009	0002	+.0005	51	173.1	0058	—·0043	0031
15	136.4	0008	0001	+.0003	52	173.4	0059	0044	0032
16	137.5	0016	6003	0005	53	173.9	-0056	0041	0029
17	137.7	0050	0013	0009	54	174.0	0055	0040	- · <b>0</b> 028
18	138.6	0006	+.0001	+.0002	55	175.3	- 0060	0045	-·00 <b>34</b>
19	142.0	0009	-0002	+.0005	56	175.5	0060	0045	0034
20	142.2	0016	-·0009	0002	57	179.3	+.0016	+.0031	+.0044
21	142.5	-·0036	0029	0025	58	179.6	+.0013	+.0058	+:0041
22	143.4	+.0005	+.0003	+.0013	59	179.6	+.0021	+.0036	+.0049
<b>23</b>	144.3	0018	0025	-0021	60	180.0	+.0013	+.0028	+ .0041
<b>24</b>	144.3	0013	0006	0005	61	183.2	.0000	+.0015	+.0029
25	145.3	+.0003	0004	+.0001	62	183.5	+.0002	+.0050	+ .0034
26	145.4	0014	0021	0016	63	183.7	+.0002	+.0020	+.0034
27	145.6	0028	-·0035	0030	64	183.7	0011	+.0004	+.0018
<b>28</b>	146.5	0002	<u> </u>	0004	65	186.0	+.0020	+.0032	+.0020
29	147.6	0030	0037	0032	66	186.0	+.0056	+.0041	+.0059
30	149.0	+.0014	+.0007	+.0012	67	187.9	+.0009	+.0024	+.0040
31	150.2	+.0002	0005	+.0003	68	188.5	+0026	+.0041	+.0028
32	153.5	0020	0035	0029	69	188.2	+.0002	+.0020	+.0037
33	154.1	0020	0035	0058	70	193.8	+.0006	+.0021	+.0040
34	155.1	0060	0025	0019	71	194.2	0022	0007	+.0012
35	155.2	0060	0045	0039	72	194.7	0008	+.0001	+.0027
36	155.2	0028	0013	- 0007	73	194.8	+.0001	+.0016	+.0036
37	155.3	0044	0029	-0023					

It is at once evident what a remarkable jump takes place at number 32. Previous to this the deviations have been both positive and negative, mostly negative, and have averaged under 0.2 per cent. Now the deviations are all negative and rarely under 0.4 per cent. But the reason for this is evident from a glance at Regnault's tables. From number 25 to 32 the calorimeter temperatures are very nearly constant, averaging 11°.5 and 23°.5, or the results are in  $c_n$  as a unit. Now if, as we have seen to be almost certain, Regnault's thermometric scale is that of the air-thermometer, and if we express everything in terms of the specific heat at 15° as a unit, these total heats should be a little large, since the specific heat at 17° is less than that at 15°. And it is to be noticed that three of the seven deviations in the experiments cited are positive. From precisely 32 on, however, the calorimeter measurements have all very nearly  $4^{\circ}$ .5 for the lower temperature and 18° for the upper, and the quantities of heat are therefore expressed in terms of  $c_{11}$ . Accordingly the total heats from 32 on are about 0.2 per cent too small and should be increased by that amount. This greatly smooths out the break at that place.

This point is also verified by experiments 8 to 23. In 8 to 13 the calorimeter range was  $12^{\circ}5$  to  $24^{\circ}$ , hence the unit is  $c_{13}$ , and the total heats should be a little large; such is seen to be the fact. In 13 to 23 the calorimeter range was 6° to 18°, the unit accordingly  $c_{13}$ , and the quantities of heat are too small. We find in fact that all the deviations except one are negative.

The first seven experiments do not bear this out quite so well. Experiments 1 to 4 are in about  $c_{1s}$  as a unit, experiments 4 to 8 in about  $c_{1s}$ , and hence the latter should show a slightly greater negative deviation of perhaps 0.1 per cent. This is not so, but the experiments are few in number and the deviations slight.

It should be pointed out here that it is not assumed that Regnault's formula is absolutely correct, but it is simply used as giving a smooth set of values from which to estimate the concordance of the experiments.

The writer considers that the facts here brought forward still further substantiate the essential correctness of the comparison of Regnault's calorimeter temperatures with the airthermometer. Accordingly he has corrected Regnault's total heats so that they should all be expressed in the same unit,  $c_{1s}$ , and has given in the fourth column of the table on page 20 the deviations of the total heats so corrected from those yielded by Regnault's formula. It will be seen that the formula actually fits the experiments much better than it appeared, the greatest actual deviation being about 0.5 per cent. This means in the latent heats a maximum deviation of about 0.7 per cent.

Experiments 1 to 57 indicate that the formula gives values slightly too great. At 57 there is another peculiar jump of about 0.75 per cent. The explanation of this is not so evident as in the case of number 32. It lies in the fact that as the temperatures became higher the experiments became more difficult to conduct. Regnault himself says (Memoir, p. 700) that after number 60 the apparatus required frequent repairs on account of the high temperatures. It therefore appears that the highest set of experiments, from 57 on, are of less weight than the others. If we take the ten experiments commencing with 47 which lie between 170° and 176° we find for their average fractional deviation -0043, the maximum being -.0051 and the minimum -.0035, the sum of the squares of the differences from the average being almost nil. If, on the other hand, we take the remaining seventeen experiments, lying between 179° and 195°, the average fractional deviation is +.0022, the maximum +.0041, the minimum -.0007. Here the extreme differences from the average are twice as great as in the preceding, while the sum of the squares of the differences from the average is considerable, thus showing their greater unreliability, apart from Regnault's own statement to that effect.

The writer has therefore considered it proper to change these average deviations by making the total heat for  $190^{\circ}$  a little smaller than that given by Regnault's formula. The equation formed is

#### $\mathbf{H} = 603.2 + 0.356 t - 0.00021 t^2$

to hold only above 100°. In the fifth column of the table (page 20) there are given the fractional deviations of the corrected total heats from this formula. It will be seen that up to 26 the experiments are satisfied as closely as possible. From 26 to 57 the deviations gradually increase on the negative side, while from 57 to 73 they are still more marked on the positive side. But 26 to 57 are greater in number than the latter, are more consistent in themselves, and, as we have seen, are more reliable. This justifies the greater weight given to them. The average deviation in the last seventeen experiments is  $\pm$  0038. Even if the corrections due to the variation of the specific heat of water are not allowed, the formula still represents the experiments better than Regnault's.

The formula is correct at  $100^\circ$ , and I think we can say that at  $200^\circ$  it cannot be more than 0.4 per cent out, corresponding to an error in the latent heat of 0.6 per cent.

Consider now Regnault's experiments below 100°. In the first six of the twenty-three from 88° to 63° the calorimeter temperatures averaged about 7° and 19°, hence the quantities of heat are expressed in  $c_{13}$  as a unit. Experiments 7 to 13 have for a calorimeter range 9° to 21°, or are in  $c_{13}$  as a unit. The remaining experiments have the same calorimeter range as the first six. Taking account of these facts, the fractional deviations of the experiments from Regnault's formula are as given below:

	t			t			t	
1	88.11	+.001	9	81.03	004	17	17.1	008
<b>2</b>	87.83	+.001	10	80.60	005	18	70.49	001
3	85.97	006	11	80.37	<u>004</u>	19	69.70	001
4	85.24	-·005	12.	80.12	001	20	68.01	007
5	85.20	.000	$13 \cdot$	79.55	.000	21	66.30	002
6	84.88	002	14	78.28	005	22	64.33	004
7	83.08	005	15	76.50	001	23	63.02	•000
8	82.66	001	16	71.35	005	. II		

It is immediately seen that Regnault's formula gives results uniformly too great. The reason is because the formula is made to fit his experiments near  $0^\circ$ , which we shall see to be at fault. The average deviation of the formula from the experiments is  $0^{\circ}3$  per cent.

The experiments near 0° are undoubtedly incorrect. They were performed by a method different from that which was used in the remainder, and Regnault himself does not consider them so good as the others, indicating a number of causes of uncertainty (Memoir, pp. 716–719). Another source of error lies in the fact that Regnault supposed, in common with the physicists of his time, that the heat necessary to form vapor depended only on the final state of the vapor and not at all on the process by which it was formed. This error did not enter into the preceding sets of experiments, for in them the process was always one of sensibly constant pressure. In the present case, in order to produce the evaporation the pressure on the liquid was reduced, and the operation was accordingly not one of constant pressure.

In place of these unreliable experiments we have the recent accurate work of Dieterici. He found for the latent heat at 0° the value 596.8, the unit being  $c_{0-100}$ . This is the result of a very careful investigation. He made first a series of eight experiments, L varying from 595.74 to 597.29. He then made a better set, three in number, the extremes being 595.98 and 596.63. He still further improved his methods and in two experiments obtained 596.67 and 597.07. The probable error is  $\pm 0.24$  or  $\pm 0.04$  per cent. In terms of  $c_{15}$  as a unit the latent heat at 0° thus becomes 598.9. Svensson's determination is somewhat larger than Dieterici's, it being 599.92 in terms of  $c_{n-100}$  as a unit; it is probably not so correct as Dieterici's, as shown by the remarkable concordance in the observations of the latter. Both have the slight possible error due to the uncertainty of the constant of the ice-calorimeter, which we have seen to be about one-quarter of one per cent.

Griffiths' determinations were of the latent heat between  $25^{\circ}$  and  $50^{\circ}$ , the determinations at  $30^{\circ}$  and  $40^{\circ}$  15 being made with particular care. They are as follows, the unit being  $c_{\mu}$ :

t	25	30	40	40.15	49.8
$\mathbf{L}^{-}$	581.9	578.7	572.4	572.6	566.5

These give total heats lying considerably below Regnault's linear formula, in this respect agreeing with the experiments of Dieterici, Svensson, and those of Regnault himself from  $60^{\circ}$  to  $90^{\circ}$ . This strengthens the reliability of the formula we have formed for the region above  $100^{\circ}$ , it also lying below the linear formula. As any expression for the total heat must

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satisfy Regnault's determination at 100°, this being by far the most certain of any, the possibility of a linear formula is thus precluded, although it is evidently nearly such.

If we attempt to form an expression for H to satisfy Dieterici's value at 0°, Griffiths' values from 25° to 50°, and Regnault's value at 100°, it will make  $\frac{d^2H}{dt^2}$  positive instead of negative, will not agree with Regnault's determinations from 60° to 90°, and will make an abrupt break at 100° where it joins the formula for the region above 100°. If one neglects Dieterici's determination and forms a formula to satisfy Regnault's value at 100° and Griffiths' determinations, and to join smoothly with the formula above 100°, it will give a value at 0° far below Dieterici's. The writer has therefore formed the following equation, using Dieterici's value at 0°, Regnault's H at 100°, and making  $\frac{dH}{dt}$  at 100° equal to that by the formula used above 100°:

$$\mathbf{H} = 598.9 + 0.442 t - 0.00064 t^2.$$

A comparison of Regnault's experiments with this formula follows, the fractional deviations being given :

1	+.0018	6	0040	11	0029	16	0031	21	+.0002
2	+.0018	7	0040	12	+.0001	17	0061	22	0016
3	0051	8	•0000	13	+.0011	18	+.0009	23	+.0025
4	0041	9	0029	14	0037	19	+.0009		
5	+.0009	10	0039	15	+.0004	20	0050		

The agreement is far better than by Regnault's formula. Indeed a much better agreement could not be obtained by any formula which joins smoothly with one which fits the experiments above 100°. If there is a question as to which set of experiments to fit best, those above 100° or those below, the answer is immediately those above, for not only are the experiments below 100° in less concordance with one another, as shown by the deviations just tabulated, but Regnault himself says that they were more difficult to conduct, the boiling not taking place steadily, but in great puffs at intervals. The expression for H will be considered only as provisional, however; the subject of total and latent heats below 100° will be discussed again in another paper. The formula does not agree any too well with Griffiths' latent heats (adding to them  $\lambda$ ), the fractional deviations of the latter from the former being about -005.

It should be observed that this formula, as well as the formula for total heats above 100°, holds independently of the judgment made that Regnault's calorie is equal to the specific heat at 15° according to Rowland. For since we know the value of the mean specific heat from 0° to 100° in terms of Regnault's calorie by Regnault's own experiments, it follows that 598.9 expresses Dieterici's determination at 0° in the same unit as that in which 636.7 expresses the total heat at 100°, be that unit  $c_{1e}$  or not. Therefore the writer considers that the formula expresses the total and latent heats in Regnault's calorie with a maximum possible error of 0.5 per cent at the lower end.

Griffiths believes that the mean specific heat from  $0^{\circ}$  to 100° is almost exactly equal to  $c_{15}$ . He bases this conclusion on the following considerations: He has expressed in terms of  $c_{15}$  his latent heats, already referred to, very closely by the linear formula

# L = 596.73 - 0.6010 t.

Extrapolating to 0° and 100° there are obtained 596.73 and 536.63. The first is almost exactly the value of L Dieterici has found at 0° in terms of  $c_{n-100}$ , the second is what one would get from Regnault's experiments on total heat if one supposed that  $c_{n-100}$  is equal to  $c_{15}$  and that Regnault's total heat at 100° is expressed also in terms of  $c_{15}$ . Thus to support a linear formula, which type of formula is improbable in itself, he has to make two suppositions, one that  $c_{n-100}$  is the same as  $c_{15}$ , which we have seen is not the best value, and the other that Regnault's calorie is equal to  $c_{15}$ , which we have seen to be probably true. But these two assumptions are contradictory, for by Regnault's own experiments on the specific heat of water  $c_{n-100}$  is 1.00358 times his calorie.

From the formulæ for h and H the writer has obtained the latent heats and thence the specific volumes of dry saturated steam. In obtaining the latter there are also required the specific volumes of liquid water at various temperatures, the relation between the pressures and temperatures of dry saturated steam, and the value of the mechanical equivalent of heat. The specific volume of water below 100° is for as many decimal places as have been used constantly 0.001 cubic meters per kilogram. Above 100° Hirn's\* formula has been adopted. For the relation between pressure and temperature Regnault's formula H has been used above 100°, while below 100° his formula C (with the constants as recalculated by Zeuner) is These should be sensibly correct except below 40°, taken. where an error exists due to the fact that Regnault did not know of the sudden change in  $\frac{dp}{dt}$  at 0°. The value of the mechanical equivalent is taken as 427.03 kilogrammeters (at

\* Ann. de Chimie et de Phys. (4), x, p. 32, 1866.

Paris) at 15° C., according to Rowland. This determination has been strongly corroborated by recent experiments.\* The volumes follow:

$\mathbf{v}^{t}$	0	10	20	30	40	50	60
	208.94	107:88	58:505	33·198	19:637	12:063	7.6703
$_{\rm V}^t$	70 5.0320	80 3·3942	90 2·3464	100 1.6587	110 1.10 1.1973	12000 0.88099	130 0.65948
$v = \frac{t}{V}$	140	150	160	170	180	190	200
	0·50152	0·38707	0·30278	0·23982	0·19216	0·15566	0·12739

Consider the possible errors in these. They may first have an error of not exceeding one-half of one per cent due to the determination of Regnault's calorie in kilogrammeters; however much this may be, it is constant for all the V's. Aside from this there may be an additional error due to our uncertainty as to the latent heats. This amounts to  $\pm 0.6$  per cent at 200°, is practically zero at 100°, and is  $\pm 0.5$  per cent at 0°. Below 40° the V's are entirely uncertain owing to the errors there in p and  $\frac{dp}{dt}$  already mentioned.

In volumetric experiments on steam there is an unusual amount of difficulty on account of condensation on the walls of the vessel containing it. This condensation increases very rapidly as the saturation line is approached, and as a consequence all direct determinations of saturation volumes are far less reliable than those calculated from the latent heats, for Regnault so arranged his experiments that this source of error was entirely avoided. An exception should be made of the determination of the volume at 0° by Dieterici, + in which more confidence can be placed, not only from the concordance of his results, but also from the fact that corrections were

made for condensation. On superheated steam experiments have been made by Regnault,‡ Fairbairn and Tate,§ Hirn, Horstmann,¶ Herwig,\*\* Meyer,+† Battelli,‡‡ and Ramsay and Young.§§ A large number of observations prior to Regnault's are not included here; these are all at very low pressures, hence large volumes, for which the substance can be treated as a perfect gas.

\* Johns Hopkins Univ. Circular No. 135, June, 1898, p. 54.

† Wied. Ann., xxxviii, p. 1, 1889.
‡ Mem. of the Inst. of France, vol. xxi, p. 700, 1847.

§ Phil. Trans., clii, p. 591, 1862.

|| Théorie Mécanique de la Chaleur.

Liebig's Annalen, Supplemental Band, vi, p. 51.

\*\* Pogg. Ann., exxysii, p. 592, 1869. +\* Chem. Berichte, 1877, p. 2068. +\* Mem. R. Acc. Sc. Torino, (2), xliii, 1893.

§§ Phil. Trans., clxxxiii A, p. 112, 1892.

For comparison of the experiments the following principles have been used:  $\frac{pv}{T}$  should never exceed its limiting value for indefinite superheating; for two experiments in which the pressures and temperatures do not differ much,  $\frac{pv}{T}$  should be almost the same (it would be constant for a perfect gas);  $\frac{pv}{T}$ at constant pressure should be greater at greater volumes or temperatures, at constant volume it should be greater at greater temperatures or pressures, and at constant temperature it should be greater at greater volumes or lower pressures. The best determination of the limiting value of  $\frac{pv}{T}$  as calculated from the chemical composition of water is that given by Van Laar,\* but since he places the absolute zero at  $-273^{\circ} \cdot 2$  C. instead of  $-273^{\circ.7}$ , the writer has modified his value to correspond, the number obtained being 3.4673, under the assumption that p is in millimeters of mercury and v in cubic meters per kilogram. In this manner the writer has made careful comparisons of the various experiments. Those of Regnault were all at such low pressures that the substance should behave as a perfect gas, which probability is well corroborated by them. The single determination of Meyer is evidently incorrect, as it gives a value of  $\frac{p\sigma}{T}$  of 3.472 in a region where the deviation from a perfect gas should be fully two per cent. The experiments of Fairbairn and Tate have in general pressures far lower than those of the others, but temperatures nearly as high; accordingly  $\frac{pv}{T}$  should be much greater, whereas it runs far less. Of their twenty-three experiments six are comparable by the preceding principles with those of Hirn,

comparatie by the preceding principles with those of Hirn, Horstmann, Herwig and Battelli, four more with those of Hirn, Horstmann and Herwig, four with Herwig and Battelli, and four either with Herwig or Battelli. In almost every case the values of  $\frac{pv}{T}$  run from two to five per cent less than they should for any agreement whatsoever, and accordingly there must have been considerable condensation.

Hirn's experiments yield great discrepancies among themselves. In seven of his twenty-two experiments, in which  $\frac{pv}{T}$ should steadily increase, the values run 3:376 3:390 3:366 3:367 3:337 3:345 3:398

\* Zeitschr. für Phys. Chem., xi, p. 433, 1893.

Similarly the numbers should increase in each of the following columns :

3.347	3.341	3.350	3.361
3.382	3.320	3.382	3.362
3.392	3.286	3.355	3.345
3.362	3.361	3.337	

There are a few other discrepancies, but these involve one-half of his experiments, and it is difficult to get any concordance by throwing out a few of the experiments. That there was a tendency towards condensation is shown by the fact that in

four of his experiments the value of  $\frac{pv}{r}$  is less than is given by

the saturation line for the same pressure, the difference being more than can be allowed by any error in the latter.

Suppose we ascribe these discrepancies to condensation, throwing out accordingly about nine experiments. The remainder are so few that they are only useful as a corroboration of others. Three of them are comparable with both Horstmann and Battelli and deviate from Horstmann about one per cent, from Battelli about one-half per cent, and this is in a region where the deviation from a perfect gas is only about  $2\frac{1}{2}$  per cent. Five others are comparable with Battelli. Of these two are in agreement, one deviates about  $\frac{1}{2}$  per cent, and the other two deviate 2 per cent. In the last two the total deviation from a perfect gas is about 6 per cent.

Of Horstmann's four experiments one is shown to be incorrect by a comparison with the others. The remaining three agree fairly well with Battelli.

Herwig himself discards fifty-five of his seventy-five experiments as showing condensation due to too near an approach to the saturation line. Of the remaining twenty, fourteen are in a region where the substance should behave sensibly as a perfect gas. Of the other six, five are comparable with Battelli. Two are in agreement, while the other three give deviations of 0.6 per cent, 1 per cent, and 2.5 per cent.

We thus see as general conclusions from the foregoing that among the experiments of Regnault, Fairbairn and Tate, Hirn, Horstmann, Herwig and Meyer, we have available thirteen by Hirn, three by Horstmann, and six by Herwig. So many of Hirn's and Herwig's had to be thrown out as to render the others doubtful, but even accepting them we have found that in the only comparisons which can be made, those of Horstmann and Hirn, there is some disagreement, and the experiments are not sufficiently numerous to give an accurate idea of the deviation of steam from a perfect gas in various regions. Nor are they useful as corroboration of Battelli's experiments, for of the twenty-two only seven agree with his, six are not comparable, four disagree slightly, and five disagree completely.

We have thus left only the experiments of Battelli and those of Ramsay and Young. Some at least of the determinations of the former at low pressures are incorrect, for they give values of  $\frac{pv}{T}$  which differ too much from a perfect gas. In the case of Ramsay and Young we are confronted by a difficulty at the very start. I take the following quotation from them (reference, p. 122):

"The weight of the water in the tube was ascertained by determining the products of pressure and volume, altering the volumes; and this was repeated at different temperatures. Assuming that if these products for any one temperature were constant, the density of the steam was constant, viz: the theoretical density, 9, the weight could be ascertained by the equation

W =  $\frac{\text{Vapor density} \times p. v \times 273}{11 \cdot 1636 \times 1000 \times 760 \times (273 + t)}.$ 

This expression simplifies to

 $\log W = \log p. v + \bar{4} \cdot 46179 - \log (273 + t).$ 

"During the progress of the experiments it happened that a trace of water passed up the tube, adding itself to that already present. This, of course, increased the weight, hence new measurements were made to determine the amount of the increase."

Thus were made the determinations of the weight of water in the tube, one the mean of experiments where the temperatures were 220° and 230°, the pressures ranging from  $2500^{mm}$ to 3800, in the second the temperatures were 230°, 240° and 250°, the pressures ranging from 2600 to 4000, and in the third the temperatures were 250°, 260°, and 270°, the pressures ranging from 2800 to 4300. Now evidently at such pressures and volumes (the greatest specific volume came out 0.676) it is impossible that the steam can be in the condition of a perfect gas, and accordingly the determination of the weight in each of the three series is incorrect, and the volumes given by Ramsay and Young should be diminished. The errors in the three sets are probably very close to the same amount, for although the increase in temperature would mean a decrease in the error due to the assumption that the steam comported itself as a perfect gas, nevertheless the specific volumes in the three sets used for the determination of the weight diminished enough to offset this.

Assuming then this constant error in Ramsay and Young's determinations, let us make a comparison of such of them as

lie near Battelli's with his. Below is given a table of the fractional deviation, d, of  $\frac{pv}{T}$  according to Battelli from that according to Ramsay and Young; in each case the experiments compared had very nearly the same values of p and T. Above each value of d is given a number for reference.

No. d	1 + .009	2 + .006	$^{3}_{+.020}$	$^{4}_{+.021}$	5 	6 + .003	7 + .005
No. d	8 + .010	9 + .027	10 + .090	11017	$     \begin{array}{r}       12 \\       - \cdot 013     \end{array} $	13016	14015
No. d	$     15 \\     - \cdot 014 $	$\begin{array}{c} 16 \\ - \cdot 007 \end{array}$	17 + .013	18 —·021	19 019	20 `020	21 • 017
No. d	$\overset{22}{-\cdot012}$	23 020	$\begin{array}{c} 24 \\ - \cdot 023 \end{array}$	25 •030	$\begin{array}{c} 26 \\ - \cdot 012 \end{array}$	$\begin{array}{c} 27\\0\end{array}$	28 + .009

Nos. 2, 3, 4 were all at one temperature, about  $150^{\circ}$  C., while 5 to 11 were at  $180^{\circ}$ , 11 to 18 at 200°, and the remainder at 230°.

The sudden changes in the values of d in 9 and 10 from those in 5 .... 8, in 16, 17 from those in 11 ... 15, and in 26, 27, 28 from those in 18 .... 25, can all be accounted for by condensation, since Ramsay and Young's figures, as will be shown, give marked evidence of condensation as the saturation line is approached, while those of Battelli do not. But the remarkable fact is that in the first eight, with the exception of the fifth, the deviations of Battelli from Ramsay and Young are all positive, the reverse of what is due to the error in the latter already mentioned. Suppose we ascribe this to large condensation in the case of Ramsay and Young. Looking at 11....28 we see that the constant error in their experiments must amount to 1.5 per cent, hence in the first eight there must have been condensation to the amount of 2.5 per cent.

But there are a few experiments below 100° which can be compared, and in that region Ramsay and Young's experiments do not have the constant error already mentioned, the weights being measured directly. These follow:

	Rams	ay and Young	Battelli.			
p	45.47	39.95	35.3	67.57	85.32	100.27
v	26.06	30.12	33.57	17.851	14.1326	12.0335
Т	348.7	348.7	348.7	352.24	352.24	352.24
$\frac{pv}{T}$	3.415	3.454	3.399	3 424	3.423	3.422

Now Ramsay and Young observed that there was far more condensation below 100° than above, so much so that they themselves admit that the larger part of their low temperature

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determinations are worthless. Therefore those given above should have at least 2.5 per cent condensation; hence, Battelli's  $p^{pv}$ .

determinations being correct,  $\frac{pv}{T}$  by Ramsay and Young should

be, perhaps not 2.5 per cent smaller than by Battelli, for the latter's volumes are smaller, but certainly 1.5 per cent smaller. Instead of that the smallest of Ramsay and Young's is only 0.8 per cent smaller than the greatest of Battelli's, while one of them is larger than any of the latter. We thus see that the supposition that the deviations in  $1 \ldots 8$  are due to condensation on the part of Ramsay and Young involves us in difficulties. At any rate they show conclusively that in the region considered either Ramsay and Young or Battelli is entirely in error.

Further, Ramsay and Young's experiments  $11 \ldots 28$  have all the same weight of water with the exception of Nos. 20 and 22, and hence should have a practically constant deviation to check with Battelli's. Nos.  $11 \ldots 15$  have such a constant deviation of about 1:5 per cent, while Nos. 18, 19, 21,  $23 \ldots 26$  have a fairly constant deviation of about 2 per cent, different from the former. Hence we see that the two investigations are entirely out of accord. One of them is incorrect, perhaps both.

We will therefore next examine Ramsay and Young's experiments by themselves. First they discard all their experiments below 75° C. as untrustworthy. At 75° their determinations show consecutive variations as high as 1.6 per cent. Above 100° C. there was a great deal of condensation in every case as the saturation line was approached; this is shown by the rapid increase of vapor density with increasing pressure. Thus at 140° C. total condensation occurred at a pressure of  $2645^{\text{mm}}$ ; the saturation pressure for that temperature is 2717. At  $150^{\circ}$ ,  $160^{\circ}$ ,  $180^{\circ}$ ,  $190^{\circ}$  and  $200^{\circ}$  total condensation occurred at pressures of 3442, 4571, 7444, 9337 and  $11505^{\text{mm}}$  respectively; the corresponding saturation pressures are 3581, 4651, 7546, 9443and  $11689^{\text{mm}}$ . Aside from this the density showed an impossibly rapid increase before condensation.

There are some other discrepancies in Ramsay and Young's observations which will merely be mentioned. Thus if comparison is made of those experiments at temperatures 270°, 260° and 250° for which the volumes are given as 0.644, 0.585, 0.529, and 0.435, it will be found that at constant volume  $\frac{pv}{T}$  decreases with increasing temperature, which is impossible. The experiments below 250° at these same volumes, as well as at others, make  $\frac{pv}{T}$  at constant volume increasing with increasing with increases.

ing temperature, which is correct; but the increase is so rapid as to look a little suspicious. According to Battelli the increase is very slow.

Even if Ramsay and Young's experiments are substantially correct far from the saturation line, they cannot be used, for they contain a constant error, the incorrect determination of the weight of water present in the tube. There is no agreement with Battelli by which this error can be estimated, nor can we determine it from our saturation volumes already obtained, since in Ramsay and Young's experiments near the saturation line great condensation occurred.

We have left therefore only Battelli. In a table below is given a comparison of  $\frac{pv}{T}$  according to such of his experiments as lie near the saturation line with that according to Regnault's experiments, the volumes being calculated from the latent heats. Each of the latter is given immediately under that one of Battelli's which is to be compared with it, and the fractional deviation of  $\frac{pv}{T}$  is given last.

$_{\mathrm{T}}^{p}$	129·14 330·7	330·78 352·2	749.12 373.33	2060·1 404·01	$3061.9 \\ 417.94$	7971·4 456·6	12181 • 475 • 71
$\frac{pv}{T}$	3.413	3.411	3.392	3.373	3.320	3.276	3.210
$_{\mathrm{T}}^{p}$	148·79 333·7	$354.62 \\ 353.7$	760 373 <b>·</b> 7	$2030.3 \\ 403.7$	$2717.6 \\ 413.7$	7546·4 453·7	$\frac{11689}{473.7}$
$\frac{pv}{T}$	3.420	3.403	3.373	3.317	3.294	3.196	3.143
d	005	+ .005	+ .006	+.012	+.012	+ .024	+ .021

It is at once seen that the discrepancy is very bad. Were the deviations negative instead of positive they could be ascribed to condensation in the case of Battelli, and his experiments not near the saturation line would still be available. Let us now see, supposing Battelli to be correct, where an error in our saturation volumes can be placed. We have seen that the greatest error which can possibly be ascribed to the mechanical equivalent of Regnault's calorie is 0.5 per cent. This would make the deviations respectively

-.007 -.003 +.001 +.012 +.012 +.019 +.016Further we have seen that the latent heat at 200° C. may be at most 0.6 per cent too small, although at 100° C. it is correct. Allowing errors in the latent heats the deviations become

 $-\cdot 007 - \cdot 003 + \cdot 001 + \cdot 010 + \cdot 010 + \cdot 014 + \cdot 010$ The two negative ones, at low pressures, could be ascribed to condensation on Battelli's part, but the remainder of course cannot.

So far we have assumed Regnault's p and  $\frac{dp}{dt}$  to be correct, and we see it is impossible to get any agreement with Battelli. If we allow an error in Regnault's p and  $\frac{dp}{dt}$ , we must take them according to the formula Battelli gives to fit his own experiments on corresponding saturation pressures and temperatures, for we are going on the supposition that his work is correct. The change in  $\frac{dp}{dt}$  changes the saturation volumes, so  $\frac{pv}{T}$  is doubly changed. The deviations then become  $+ \cdot 023 + \cdot 006 + \cdot 018 + \cdot 007 + \cdot 013 + \cdot 019$ and things are made worse rather than better.

It is thus a question of whether to discard Regnault's data entirely, or Battelli's. Regnault's results, with the exception of total heats at low temperatures, have received essential corroboration from almost every one who has gone over the same ground, and this is especially so concerning saturation pressures and temperatures. On the other hand, Battelli's saturation pressures deviate considerably from those of all other observers, we have seen that in some of his volumetric experiments at low pressures errors exist, and that finally there is practically no corroboration between his volumetric experiments and those of other investigators.

The writer therefore concludes that all our knowledge concerning the density of steam is limited to the saturation line, the experiments on superheated steam presenting discrepancies which cannot be reconciled.

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# ART. V. — The Estimation of Boric Acid; by F. A. GOOCH and LOUIS CLEVELAND JONES.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXVII.]

THE estimation of boric acid by treating the salts of that acid with sulphuric acid, distilling with methyl alcohol, evaporating the distillate over magnesium oxide, igniting and weighing, was proposed by Rosenbladt.\* A little later, and without knowledge of Rosenbladt's experience, a somewhat similar process,<sup>†</sup> which consisted in the treating of the compound of boric acid with acetic acid or nitric acid, distillation with methyl alcohol, evaporation of the distillate over calcium oxide, and ignition of the residue, was described by one of us. In the course of the development of this process, it transpired that the insolubility of magnesium oxide retards the absorption of boric acid by that substance, and that the more soluble calcium oxide retains boric acid more actively and is therefore to be preferred.

Points in the treatment upon which special emphasis was laid in the original description of this process were the choice of a suitable apparatus for the distillation, the employment of a loosely stoppered receiver for the reception of the distillate upon slaked lime, the careful removal of water from the substance in the retort before acidifying and treating with the methyl alcohol, regulated use of acid, and care in the evaporation and ignition.

The attainment of good results in this process depends upon attention to details. Modifications have been suggested by several investigators. Thus, instead of igniting the calcium oxide in a large platinum crucible, transferring it to the receiver to hold the boric acid, and returning the calcium oxide with the distillate to the same crucible for subsequent ignition of the residue, as was originally proposed, Penfield<sup>‡</sup> prefers to ignite the calcium oxide in a small crucible, to collect the distillate in ammoniacal water, to evaporate the latter over the calcium oxide in a large platinum dish, and to transfer this residue back to the small crucible for the final evaporation and ignition. Kraut§ suggests a modification of form in the apparatus with no other essential change in conditions. Moissan has suggested changes in the apparatus and avoids a transfer of the calcium oxide—collecting the distillate by itself in a closed receiver, trapped with an ammonia bulb to prevent the escape of the boric acid from the distillate. Furthermore, Moissan's process calls for the use of an amount of calcium oxide from fifteen to twenty times greater than that theoretically required.

<sup>\*</sup> Zeitschr. für Anal. Chem., xxvi, 21. † Am. Chem. Jour., ix, 23. § Zeitschr. für Anal. Chem., xxxvi, 3.

t This Journal, xxxiv, 222. Compt. Rend, cxvi, 1084.

From our experience it seems obvious that the demand for this amount of calcium oxide arises from an excessive use of nitric acid in the retort and the consequent modification of conditions in the distillate. Fortunately this difficulty may be avoided by the use of a little phenolphthalein as an indicator in the retort and care to limit the addition of nitric acid to the amount required to produce distinct acidity. The addition of a drop of the acid and another of the indicator should be repeated once or twice during the distillation to insure the replacement of the acid volatilized from the salt slightly decomposed in the process. The effect of much nitric acid is bad, not only because it neutralizes the calcium oxide when it passes to the distillate, but because when it is used a tendency is developed on the part of the dried mixture of calcium hydroxide and borate to puff explosively if this ignition is begun as soon as the residue is dry. If the residue is heated gradually and as strongly as possible over a radiator before the flame is actually applied to the crucible, no such action takes place; we are disposed to attribute it to the effect of the nitrate and nitrite, produced by the absorption of nitrous fumes in the lime, upon the alcohol or other organic matter retained by the lime in the evaporation and drying unless the latter process is prolonged at high temperature.

That good results may be obtained with small amounts of calcium oxide provided care as to the use of nitric acid and the conditions of ignition be taken, is shown by the figures of the original description and by the following experiments, in which phenolphthalein was employed as an indicator and the residue heated strongly over the radiator before actual ignition.

laO taken.	B <sub>2</sub> O <sub>3</sub> taken.	$B_2O_3$ found.	Error.
grm.	grm.	grm.	grm.
2.3405	0.1288	0.1792	+0.0004
1.7620	0.1790	0.1285	-0.0002
2.1757	0.1824	0.1840	+0.0016
2.5656	0.1788	0.1786	-0.0005

These results are accurate within reasonable limits. On the other hand, without care to ignite gradually we have noted errors of from 0.0030 grm. to 0.0060 grm. in the process otherwise conducted similarly. Doubtless the use of large amounts of calcium oxide as suggested by Moissan may serve the purpose of diffusing the explosive mixture through a mass of inert matter sufficient to prevent violent puffing, but care to heat over the radiator as strongly as possible before opening the flame directly to the crucible answers the same end. The difficulty does not exist when acetic acid is used in place of nitric acid, though even in this case it is safer to use the radiator in the first stages of heating, thus avoiding the danger of mechanical loss by too rapid ignition.

Following are determinations made by this method with the use of acetic acid.

CaO taken.	B <sub>2</sub> O <sub>3</sub> taken.	B <sub>2</sub> O <sub>3</sub> found.	Error.
grm.	grm.	grm.	grm.
0.9977	0.5062	0.2062	-0.0003
1.0220	0.2067	0.2070	+0.0003
1.3717	0.2077	0.2075	-0.0005
1.1310	0.1291	0.1795	+0.0004

The results of the preceding table, as well as those of the investigators mentioned, are a sufficient answer to the criticism of Reischle,\* that acetic acid and nitric acid do not liberate boric acid in the distillation process so that good results may be obtained. Moreover, it has been shown by one of ust that even carbonic acid is strong enough to bring about complete volatility of boric acid with methyl alcohol.

# The use of Calcium Oxide as a Retainer.

Quite recently Thaddeeff<sup>‡</sup> has advocated the abandonment of calcium oxide as an agent for holding boric acid in the evaporation of alcoholic and aqueous solutions on account of the hygroscopic nature of the oxide and the consequent difficulty of securing it in definite conditions for weighing, and proposes, instead of using calcium oxide, to retain and estimate boric acid in solution by converting it into the form of potassium borofluoride.

In the final modification of Thaddeeff's method the proposal is made to liberate the boric acid from its compounds by sulphuric acid, to volatilize it in methyl alcohol with the aid of a current of dry air, to catch the distillate in potassium hydroxide, to treat the mixture of hydroxide and borate with hydrofluoric acid in excess and evaporate in the steam bath, to digest the residue of fluoride and borofluoride at normal temperatures for two hours with 50<sup>cm<sup>3</sup></sup> of a potassium acetate solution (sp. gr. 1.14) and for twelve hours more after adding 100<sup>cm<sup>3</sup></sup> of ethyl alcohol (sp. gr. 0.805), to filter on paper, wash the residue with 62-72<sup>cm<sup>3</sup></sup> of alcohol (sp. gr. 0.805), dry at 100° and weigh as potassium borofluoride, after which the borofluoride is to be dissolved in boiling water and tested with calcium chloride for possible contamination by the presence of a fluoride. Plainly Thaddeeff's procedure presents at the outset difficulties; for besides the inconvenience of conducting long digestions with reagents of regulated strength, the difficulty of procuring hydrofluoric acid free from silica, which if present (as it usually is, in the so-called chemically pure hydrofluoric acid of commerce) would be retained in the borofluoride as potassium

\* Zeitschr. für Anal. Chem., xxvi, 512.

† Jones, this Journal, v, 442. ‡ Zeitschr. für Anal. Chem., xxxvi, 568.

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fluosilicate, the inaccuracy of the dried paper filter, and the obvious uncertainty of success in an attempt to wash a mixture of acid potassium fluoride and potassium borofluoride in potassium acetate and alcohol, so that the one shall be rendered entirely soluble while the other remains sensibly unaffected,besides these objections, there is the theoretical probability that boric acid must be lost by volatilization during the evaporation of the solution of the mixed salts in the presence of free hydrofluoric acid. This last point was put to the proof by submitting to distillation in a platinum retort a mixture of equal quantities of borax and potassium hydroxide with an excess of hydrofluoric acid, collecting the distillate in potassium hydroxide, evaporating it to dryness and testing it for the presence of boric acid. When this residue from the evaporated distillate was treated with sulphuric acid and methyl alcohol, the burning alcohol vapor gave plainly the green flame of boric acid. Another portion showed clearly the presence of boric acid when acidulated with hydrochloric acid tested with turmeric paper. No boric acid could be detected in any of the reagents used. It is plain, therefore, that boric acid does volatilize upon the evaporation of a mixture of potassium fluoride and borofluoride in acid solution. The amount of such loss is disclosed in the record of the following experiment. Portions of a standard solution of boric acid, prepared by dissolving a known weight of anhydrous boric oxide in a liter of water, were mixed with a solution of potassium hydroxide (free from silica and standardized by conversion to the chloride) in the proportions to form the potassium borofluoride, and an excess of hydrofluoric acid was added. The mixture was evaporated and the residue was dried and weighed at 100°, the whole operation being conducted in platinum.

HKF <sub>2</sub>		KFBF <sub>3</sub>		Error in	Error in
equivalent to	$B_2O_3$	theoretical	KFBF₃	terms of	terms of
KOH taken.	taken.	weight.	found.	KFBF <sub>3</sub> .	$B_{2}O_{3}$ .
grm.	. grm.	grm.	grm.	grm.	grm.
0.3231	0.1582	0.5701	0.5580	-0.0151	-0.0033
0.3192	0.1430	0.5154	0.5100	-0.0054	-0.0012
0.3192	0.1430	0.5154	0.2030	-0.0154	-0.0034
0.3192	0.1430	0.5154	0.5088	-0.0066	-0.0018
0.3192	0.1430	0.5154	0.5114	-0.0040	-0.0011

In experiments (1) to (3) the volume of the solution evaporated was about  $50^{\text{em}3}$ . In experiment (4) this volume was reduced about one-half before acidifying with hydrofluoric acid, while in experiment (5) the solution was diluted about one-half before adding the hydrofluoric acid. It is plain, therefore, that in this single step of Thaddeeff's process there is a considerable error of deficiency. On the other hand, the errors for the full process as laid down by Thaddeeff have been in our experience invariably differences of excess—presumably because the loss due to volatilization of boric acid has been overbalanced by the inaccuracy in washing. It is plain that the process can give true indications only by the balancing of considerable errors.

If we take into consideration, therefore, the inevitable inaccuracy and inconvenience of Thaddeeff's proposal, it cannot be regarded as a desirable substitute for the process according to which boric acid is absorbed and retained for weighing with calcium oxide, especially since the difficulties in the way of getting constant weights of that substance are by no means insuperable.

Thus the following table shows the series of weights taken in several experiments in bringing calcium oxide to a constant weight in a 50<sup>cm<sup>3</sup></sup> platinum crucible ignited over a blast lamp, as well as the weight taken after adding a known amount of standard boric acid solution to the slaked oxide, evaporating, and igniting. The results recorded are those of experiments made on days not moist beyond the average and with the greatest care to approach the limit of accuracy with which calcium oxide and the boric acid held thereby can be weighed under ordinarily favorable conditions. The first weight of calcium oxide recorded under each experiment was taken after a strong ignition over the blast lamp for about one-half hour. The succeeding weights were taken after similar ignition of five minutes. In all cases the crucible was left to stand a definite period in a sulphuric acid dessicator, and, after the approximate value had once been obtained, the weights of the preceding weighing were replaced on the balance before the crucible was taken from the dessicator. The average of the weights bracketed is the weight taken as constant for the calculations.

	CaO	$B_2O_3$	$CaO + B_2O_3$	$CaO + B_2O_3$	
	taken.	taken.	taken.	found.	Error.
	grm.	grm.	grm.	grm.	grm.
	0.9505			1.1590) .	
(1)	0.9493) 0.9493	0.2095	1.1588	1-1591 (1.1591	+0.0003
(1)	0.9493			, i	
	1.1319			1.3499	
	1.1317)			1.3474)	
(2)	1.1313 21.1315	0.2150	1.3465	1.3475 \ 1.3475	+0.0010
( )	1.1315)			1.3476)	
	0.8028			0.9205	
(3)	0.8025 ) 0.8024	0.1184	0.9208	0.9206) 0.9206	+0.0005
` '	0.8024 ∫			0.9206 ∫	
	2.6980				
(4)	2.6975			2.9043	
. /	2.6973 ) 2.6973	0.2073	2.9046	2.9049 2.9048	+0.0005
	2.6973			2.9044	

Obviously calcium oxide may be weighed with accuracy, with or without boric acid; but the fact remains that a less hygroscopic absorbent—one requiring less care in the handling, is to be desired.

# The use of Sodium Tungstate as a Retainer.

In searching for a suitable material of less hygroscopicity to replace calcium oxide as a retainer for boric acid, we have found that sodium tungstate, fused with a slight excess of tungstic acid over that contained in the normal tungstate (to insure its freedom from carbonate), answers this purpose excellently. This substance is definite in weight, not hygroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. To test its value as a retainer for boric acid, portions of it—4 to 7 grms.—were fused and weighed in a 50<sup>cm<sup>s</sup></sup> crucible, the tungstate was dissolved in water and to it was added a known amount of a standard solution of boric acid. After diluting, mixing, evaporating, and fusing the residue, the increase in weight should represent the boric anhydride held by the tungstate. The results of the accompanying table show how accurately the boric acid is retained under these conditions: In experiments (3) to (7) the tungstate, after its first weighing, was dissolved, transferred to a larger platinum dish and mixed therein with the boric acid. After evaporation to a suitable volume this solution of tungstate and boric acid was transferred to the original crucible for final evaporation and ignition.

	<u> </u>		
$Ma_2WO_4 + WO_3$	$B_2O_3$	$B_2O_3$	Error
taken.	taken.	found.	in $B_2O_3$ .
grm.	grm.	grm.	grm.
6.5416	0.1784	0.1771	-0.0013
7.3134	0.1786	0.1773	-0.0013
5.5003	0.0950	0.0952	+0.0005
4.1394	0.0944	0.0944	0.0000
7.5037	0.2148	0.2149	+0.0001
4.7744	0.2718	0.2702	-0.0016
6.6470	0.2503	0.2487	-0.0016

It is plain that though the sodium tungstate does not hold the boric acid with absolute accuracy the errors are not unreasonable -0.0008 grm. in the mean. Upon substituting the tungstate for calcium oxide as a retainer in the distillation process, the results were likewise highly favorable.

We used by preference the apparatus originally proposed, excepting that the Erlenmeyer flask used as a receiver is fitted tightly to the condenser and trapped with water bulbs. The retort is made very easily from a 150<sup>cms</sup> pipette and has the special advantage that particles of the residue spattering dur-

ing distillation are easily washed from the walls of the vessel by a slight rotary motion of the retort. It was found that special care should be taken to give the tungstate ample time for contact with the distillate before exposing the latter to atmospheric evaporation. The distillate was received, there-fore, in a dilute solution of sodium tungstate placed in the receiver, cooled by ice and trapped with water, and the mixture was well stirred, allowed to stand one-half hour, evaporated to small volume in a large dish, and transferred to the crucible in which the tungstate had been originally weighed. After thorough drying the residue was ignited to fusion and weighed. When acetic acid was employed in the retort, care was taken in the ignition to expose the fused mass freely to the air (by causing it to flow upon the sides of the crucible) until the color of the cooled tungstate was white, in order that the reducing effect of the acetate might be eliminated. In the experiments recorded in the following table the tungstate was used in the receiver to retain the boric acid distilled as usual with methyl alcohol, from the borates treated with acetic acid, nitric acid or sulphuric acid, in amounts regulated by the use of phenolphthalein as an indicator.

$B_2O_3$	$B_2O_3$	
taken.	found.	Error
grm.	grm.	grm.
With Ni	tric Acid.	
0.1582	0.1572	-0.0010
0.1329	0.1323	-0.0006
0.1267	0.1256	-0.0011
With Ac	etic Acid.	
0.1434	0.1418	-0.0016
0.1431	0.1433	+0.0002
0.1589	0.1587	-0.0005
0.1433	0.1422	-0.0011
With Sulp	huric Acid.	
0.1282	0.1579	-0.0003
0.1582	0.1577	-0.0002
0.1265	0.1264	-0.0001
0.1392	0.1390	-0.0005
	B <sub>2</sub> O <sub>3</sub> taken. grm. With Ni 0·1582 0·1329 0·1267 With Ac 0·1434 0·1431 0·1589 0·1433 With Sulp 0·1582 0·1582 0·1582 0·1582 0·1265	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Excessive use of acid is disadvantageous, and this is especially true in the case of sulphuric acid; for, if this acid is carried over with the methyl alcohol, as it is at 100° if present in appreciable excess, a part of it, at least, is held permanently by the tungstate to increase the apparent weight of the boric acid to be estimated.

The manipulation of the tungstate presents no difficulties, and the results obtained by its use are reasonably accurate.

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# ART. VI.—Descriptions of imperfectly known and new Actinians, with critical notes on other species, II.; by A. E. VERRILL. Brief Contributions to Zoology from the Museum of Yale College, No. LIX.

### Family HALOCLAVIDÆ Ver. nov.

COLUMN much elongated, either smooth or with suckers; base with a very small or rudimentary disk; tentacles 20, obtuse or capitate; ten pairs of mesenteries, all perfect.

### Haloclava, gen. nov. Type H. producta (Stimp.) Ver. Figure 7.

Column much elongated, soft, without a sheath, the upper part with rows of distinct adhesive suckers. Upper end with a sphincter and capable of involution. Aboral end often inflated or bulbous, with a rudimentary disk, capable of adhesion to small pebbles. Tentacles twenty, short, usually clavate, nearly equal, marginal. Mesenteries very muscular, all perfect,



#### Fig. 7.

arranged in 10 pairs; six of these pairs are larger and form a regular primary cycle; four other pairs, narrower below, belong to the second cycle; the usual pair, next to the ventral or sulcar pair of directives, is lacking on each side.

Besides the type species this genus will include *H. albida* Ver., which I now consider only a variety. *H. Capensis* Ver., Commun. Essex Inst., v, p. 5, pl. 3, fig. 7, 1869; *H. brevicorris* (Stimp.) Ver., op. cit., p. 4, pl. 3, figs. 2, 2<sup>a</sup>, 2<sup>b</sup>; and *H. Stimpsoni* Ver., op. cit., p. 5, pl. 3, fig. 1, 1869, resemble this genus but probably belong to *Eloactis* Andres. No specimens

\* Andres, in his classical work on the Actinaria, has entirely overlooked my two illustrated articles on Actinaria of the North Pacific Expl. Expedition, in the Comm. Essex Inst., vols. v and vi, 1868, 1869, quoted above, and has, therefore, omitted one of the above named species from his work, as well as numerous other species and several genera first described and illustrated in those papers. In several cases he stated that no figures nor descriptions of certain species therein described had been published. Nevertheless he quotes those papers in his bibliography. In the papers referred to there are four plates of Actinic (40 figures). He also failed to quote several other papers by me. Among those omitted are Report on Invert. of Vineyard Sound, etc., 1874; Radiata from Coast of North Carolina, this Journal, iii, p. 423, 1872; Bulletin, U. S. Nat. Mus., No. 15, 1879; American Naturalist, ii, p. 251, and several others. He intended to include all the literature and all known species. Such omissions are liable to happen in the best works. of either species were preserved by Dr. Stimpson. His original drawings show no suckers.

H. producta ranges from S. Carolina to Cape Cod. Var. albida, Cape Cod.\*

*Eloactis brevicornis* and *E. Capensis* are from Cape of Good Hope.

E. Stimpsoni, Hong Kong, China.

Family BUNODACTIDÆ Verrill = Bunodidæ Gosse.

Bunodactis V., new name = Bunodes Gosse (restr.)

Bunodes (pars) Gosse, 1855, 1860, not of Eich. (genus of Eurypteroidea), 1854.

Unfortunately the name *Bunodes* was preoccupied,<sup>†</sup> as indicated above, for a genus of eurypteroids, and some other name has to be chosen for this well known genus of actinians. None of the numerous groups recently established seem to correspond with this genus, and I have, therefore, given it a new name.

This genus, as now limited, includes species that have from 12 to 48 pairs of perfect mesenteries,‡ the number increasing with age. All the larger mesenteries, except the directives may bear gonads. The submarginal sphincter is prominent, endodermal and circumscribed. The verrucæ of the column are intraseptal evaginations of the wall and serve as true adhesive suckers; some of the rows may reach the base. The wall is imperforate, at least in the typical forms. The marginal tubercles are simple and similar to those below, and are not true acrorhagi, though sometimes pigmented distinctively. The wall is thick and muscular.

Bunodactis seems to include a considerable number of species, widely distributed. Among these are the following: B. verrucosa (Penn.) = gemmacea (type); B. Balli (Cocks); B. Listeri (Johns.); B. glandulosa (Otto) = B. rigida (And.); B. thallia (Gosse); B. sabelloides (Andres), all from European seas; B. pluvia (Dana); B. cruentata (Dana); B. ocellata (Less.), and B. papillosa (Less.), West S. America; B. inornata (Ver.) Hong Kong; and B. Japonica (Ver.) Japan. In accordance with the usual custom, the change in the typical generic name will make it necessary to change the family name Bunodidæ to Bunodactidæ. Tealiadæ (Hert.) might be used, were not Tealia a synonym of Urticina (Ehr., 1834, restricted).

\* Andres has based a new sp. (H. Elizabethx) on an incorrect outline figure of this, in a popular work. It is the same as H. albida.

+ Eichwald, Bull. Soc. Imp. Nat. de Moscou, vol. xxvii. part I, pp. 50, 107, pl. II, figs. 2-4, 1854, Bunodes lunuda. The article is dated, at the end, Nov. 2, 1853. ‡ Y. and A. F. Dixon (Sci. Proc. Roy. Dublin Acad., ii, p. 310) have shown

 $\ddagger$  Y. and A. F. Dixon (Sci. Proc. Roy. Dublin Acad., ii, p. 310) have shown that in *B. thallia* the number of mesenteries and their arrangement are remarkably variable, and that abnormal specimens are found with one or with three pairs of directives and corresponding siphonoglyphs. I have found the same variations in *B. stella*, which usually has about 24 pairs of perfect mesenteries.

#### Bunodactis stella Verrill.

Bunodes stella Verrill, Revis. Polyps E. coast of U. S., p. 16, pl. I, figs. 1-8, 1864; Amer. Naturalist, II, p. 258, 1868. Bunodes spectabilis Verrill, Check List Mar. Invert. N. New Eng., p. 15, 1879;

Bunodes spectabilis Verrill, Check List Mar. Invert. N. New Eng., p. 15, 1879; Cont, to Nat. Hist. of Arctic America, in Bulletin U. S. Nat. Mus., No. 15, p. 152, 1879 (non Fabr.).

Bunodes (?) stélla Andres, Attinie Golfes von Neapel, p. 230, 1884. McMurrich, Actinaria of Bahama Is., p. 30, 1889.

Having received large specimens of this species from Greenland and Cumberland Gulf, I at one time identified it with A. spectabilis Fabr., owing mainly to the green color of the latter, but as this was not described as vertucose, it is more probable that it was the green variety of Urticina crassicornis, which also occurs in Greenland. At Eastport, Me., between tides, a common variety of the latter is green mottled more or less with red or brown.

This species is a true Bunodes, closely related to the common European species (*B. verrucosa*), as stated in my detailed description in 1864. It is somewhat singular that Andres, with my full description and figures, should have put it as a doubtful species, even suggesting that it might belong to *Aulactinia*, a genus established by myself for a species described in the same paper with the present one, as if I did not know the characters of my own genera and species!

McMurrich simply followed Andres in expressing this doubt, but regretted that he could not obtain examples for study, after futile efforts. It is, however, a very abundant species at low-water mark at Eastport, Me., and numerous specimens have been preserved by me for the Mus. Comp. Zool. (including the original types); the U. S. Nat. Mus.; the Mus. of Yale University, etc. He certainly did not ask me for specimens.

He also described a very different species, from the Bahamas, for which he proposed the provisional name of *Aulactinia stelloides*, but he, at the same time, expressed the opinion that it might prove to be identical with *B. stella*.

Mr. Duerden (Journ. Inst. Jam., ii, p. 454, 1898), misled by this statement, went farther and definitely united the same species, from Jamaica (as *Aulactinia stella*), with my *B. stella*. The latter is a very arctic littoral species, ranging from Maine to Greenland. Its occurrence as a littoral species in the West Indies would, of itself, be a case without parallel. The West Indian species probably belongs to a different genus, but it does not agree with the characters of typical *Aulactinia*.

For such species I propose the name Bunodella.

## Bunodella V., gen. nov. Type B. stelloides (McMur.)

Form of body and tentacles same as in *Bunodactis*. Column with longitudinal rows of true adhesive vertuce on the upper

part. Margin with a row of simple, round or conical verrucæ similar in structure to the others. Mesenteries in several cycles with but six perfect pairs (in the type). Submarginal sphincter well developed, endodermal, circumscribed.

<sup>\*</sup> Differs from Aulactinia in not having lobate marginal verrucæ. The structure of the column-wall is also different: From Bunodactis it differs, so far as known, in having but six pairs of perfect mesenteries, as in very young examples of the latter. Should larger specimens of Bunodella be found to have a greater number of perfect mesenteries, this group would not differ essentially from Bunodactis.

# Anthopleura Dowii Ver. Figure 8.

Trans. Conn. Acad. Sci., i, p. 474, 1869; Andres, op. cit., p. 223, 1884 (Dovii).

This species was pretty fully described by me in 1869, but the anatomy was not then given.

A medium sized example,  $40^{\text{mm}}$  across, in alcohol, has about 96 pairs of mesenteries, of which 48 are perfect and furnished with large plicated muscles along most of their breadth; a pair of very small imperfect mesenteries, without gonads, usually intervenes between each perfect pair. The mouth has two large siphonoglyphs and about 22 crenulations on each side. Sphincter muscle well circumscribed, ovate in section, not very large. Larger submarginal tubercles or actinobranchs have 4 to 6 lobules on the lower side, each with a small point, appearing as if perforated, though the openings, said to exist in life, are not visible (fig. 8). Adhesive, cup-shaped suckers, of the longer rows, reach the base. Panama to San Salvador.

## Anthopleura Stimpsoni Ver., Comm. Essex Inst., vi, p. 32, 1869. Figure 9.

This species has 12 pairs of perfect mesenteries, with large muscles along most of their breadth; 12 pairs of 3d cycle, well developed; about 24 pairs of 4th cycle, of small size and barren; all the others, except directives, bear large gonads. Sphincter muscle circumscribed, rather large, ovate in section. Actinobranchs (fig. 9) crowded, three to five in the larger rows, the upper one three to five lobed or digitate, the larger lobes often subacute and perforated. Adhesive suckers large, in unequal rows. Hong Kong, China. Type.

### Bunodosoma, gen. nov. Type, B. granulifera (Les.).

General form and appearance as in *Bunodactis*, but the hollow verrucæ, arranged in vertical rows, are rounded or subconical and do not form adhesive suckers. Upper or submarginal ones are larger and in mature specimens more or less lobulated, but have nearly the same structure as those below, though they are described as perforated when living. Tentacles numerous; many mesenteries, 12, 24, or more pairs being Sphincter muscle well developed, endodermal and perfect. circumscribed.

To this group I refer the following:

Bunodosoma granulifera (Les., 1817).

Aulactinia granulifera Andres, 1884, p. 221. Bundes granulifera Duerden, 1898, p. 454. Bundes tæniatus Mc Mur., 1889, p. 23. Cereus Lessoni Duch. and Mich., 1860, p. 42.

West Indies.

Bunodosoma cavernata (Bosc, 1801).

Bunodes cavernata Ver., 1864, p. 17. Cladactis cavernata Ver., 1869, p. 473. Phymaetis cavernata Andres, 1884, p. 231; Mc Mur., 1887, p. 51.

South Carolina to Cape Hatteras.

Various other species described under Bunodes, Aulactinia, etc., may belong here, but the descriptions of the verrucæ and other parts are insufficient to determine their position. Aulactinia crassa Andres looks more like Bunodosoma than like Aulactinia.

#### Family PHYLLACTIDÆ.

Asteractis Verrill, 1869. Type, A. Bradleyi.

Asteractis Verrill, Trans. Conn. Acad. Sci., i, p. 465, 1869. Andres, op. cit., p. 292, 1884.

This genus is characterized by the presence of a special wide ruffled collar outside the tentacles, covered with complex rows of compound verruce or lobed outgrowths,\* but not forming true free fronds. The column bears more or less numerous adhesive verrucæ in rows below the collar. There are 12 or 24, or more pairs of perfect mesenteries and one, or sometimes two, endodermal sphincter muscles.

## Asteractis flosculifera (Les.) Ver.

Actinia flosculifera Les., Journ. Acad. Sci. Philad., i, p. 174, 1817 (not Oulactis flosculifera Duch. and Mich., nor of McMurrich).

Evactis (?) flosculifera Andres, op. cit., p. 235. Oulactis fasciculata McMurrich, Proc. Philad. Acad. Sci., 1889, p. 108; also in Heilprin's "The Bermuda Islands," p. 112, pl. x, fig. 5 (section), 1889.

This species is common at Bermuda, living buried to its margin in shell-sand at low-water mark. Figures from life will be published soon in Trans. Conn. Acad. Science.

\* They are probably branchial in function and may be called actinobranchs (Actinobranchia). The groups that they form may be called pseudofronds.

It has been pretty fully described, as to its anatomy, by McMurrich. The collar is covered by radial pseudofronds



composed of about three rows each, of lobed tubercles, the lobules being short or rounded; a single larger lobed tubercle or actinobranch occupies the distal end of each group, and a nearly simple one often forms the proximal end, next to the fosse at the bases of the tentacles. The color is variable, but the collar is usually umber-brown, varied with yellowish, flake white, and reddish brown spots.

### Asteractis Bradleyi Ver. Figures 10, 11, 12.

Trans. Conn. Acad., i, p. 465, 1869. Andres, op. cit., p. 292, 1884.

This is closely allied to the preceding species. The pseudofronds of the collar are made up of more finely lobulated verrucæ, so that they appear more complex. These verrucæ, in



the alcoholic specimen, are closely crowded in each radial series, of which there are 48; their upper and lateral surfaces are divided into many small rounded or conical lobules, most prominent along the outer sides and at the distal end of the last or distal one, where about five lobules project, in each group, beyond the edge of the collar, giving it a finely serrate or fringed appearance (figs. 11, 12). The vertue form adhesive suckers are in 48 rows, of 3 to 5 each, corresponding to the pseudofronds, and extending only a short distance below the collar.

The general figure, now given, is based on a sketch from life, by F. H. Bradley, of the original type, corrected by comparison with the preserved specimen, which was from Panama.

#### Asteractis conquilega (Duch. and Mich.) Ver,

Oulactis flosculifera Duch. and Mich., Corall. Antill., p. 46, 1860 (non Les.); Supl., p. 129, 1866. McMurrich, Actin. Bahamas, p. 56, pl. II, fig. 2, pl. IV, figs. 12-14 (anatomy), 1889.

Oulactis conquilega Duch. and Mich., op. cit., pp. 49, 89, pl. VII, figs. 7, 11, 1860. Oulactis foliosa Andres, op. cit., p. 290, 1884.

The collar of this West Indian species is very broad and is covered with about 24 pseudofronds, or groups of small folds and lobulated and crowded actinobranchs, much more complex than in either of the preceding species.

### Asteractis formosa (Duch. and Mich.) Ver.

Oulactis formosa D. and M., op. cit., p. 47, pl. VII, figs. 4, 5, 1860; Supl., p. 36 (130), 1866. Andres, op. cit., p. 291.

This is closely allied to the preceding species, but has smaller and less complex groups of lobulated actinobranchs on the collar and fewer tentacles. Guadaloupe.

### Family DENDROMELIDÆ McMurrich.

Lebrunia Duch. and Mich., Corall. Ant., p. 48, 1860.

Actinodactylus (pars) Duch. and Mich., op. cit., p. 44, 1860. Stauraclis (pars) Andres, op. cit., p. 255, 1884 (new name for last). Taractea Andres, op. cit., p. 284, 1884 (for L. Danæ).

Lebrunea McMurrich, Actinaria Bahama Is., p. 33, 1889; Duerden, Actin. Jamaica, p. 456, 1898.

This remarkable genus is characterized by having a series of about six (sometimes 5 or 8) large, dichotomously branched fronds, or branchiæ (actinobranchiæ) exterior to the tentacles. The species examined by me has, on these fronds, at the forks, many more or less spherical bodies having the structure of acrorhagi. There are numerous mesenteries, most of them perfect and bearing gonads. Sphincter muscle feebly developed or wanting.

The genus Actinodactylus Duch., 1850, was based on A. Boscii D., which may, perhaps, have been only a young Lebrunia. It was only 4 to 5 lines in diameter, with 15 small, simple tentacles, in a single circle, and with 5 elongated, pedicelled, trilobed fronds, the lobes with small subdivisions. It may, however, prove to be a distinct genus when larger examples can be studied.

The second species referred to it (1860), as A. neglectus, appears to be the young of *Lebrunia neglecta*, described in the same work. Although it was only 5 lines in diameter it had 30 tentacles and 5 dichotomously branched fronds.

#### Lebrunia Dance (D. and M.) Verrill. Figure 15.

Oulactis Danæ Duch. and Mich., op. cit., p. 47, pl. VII, fig. 10 (frond), 1860. Rhodactis Danæ Duch. and Mich., Supl., p. 37, 1866. Taractea Danæ Andres, op. cit., p. 284, 1884. Lebrunea negleta Duerden, Actin. Jamaica, p. 456, 1898. ? Hoplophoria coralligens Duerden, loc. cit. (non Wilson).\*

Specimens of large size, up to 8 inches or more in diameter, were obtained by me at Bermuda, in 1898. These agree very well with the specimens described by Duerden from Jamaica, as *L. neglecta*, but not with those described by McMurrich under the same name. In having numerous rounded acrorhagi on the actinobranchs or fronds (fig. 15) my species agrees with the *Oulactis Dance* D. and M., from St. Thomas, which is evidently a *Lebrunia*, and there is no reason to doubt its identity with the Bermuda species.

My larger examples were usually dark green in life, with the tentacles somewhat paler green and flecked more or less with white; disk olive-green with whitish radial spots; fronds bluish green with the tips and rounded bodies light blue. It lives with the body concealed in holes or crevices of the reefrock, at and below low-water mark. The tentacles are long.

### Lebrunia neglecta Duch. and Mich.

Lebrunia neglecta Duch. and Mich., op. cit., p. 48, pl. VII, fig. 8, 1860 (young). Andres, op. cit., p. 362 (non Duerden).

? Actinodactylus neglectus Duch. and Mich., op. cit., p. 44, 1860 (very young).

? Stauractis incerta Andres. op. cit., p. 255, 1884 (new name for last).

Lebrunea neglecta McMurrich, Actin. Bahama Is., p. 33, pl. I, fig. 7 (general), pl. III, figs. 11-14 (anatomy).

This species was originally based on a small specimen (about one-half an inch high), but it had relatively large, much dichotomously divided fronds, according to the figure. McMurrieh has given a detailed description of a species that appears to be the same, though much larger in size. His figures represent the 6 fronds as dichotomous, but with few divisions, though in

\* The Hoplophoria coralligens Wilson, was described from a single, very small specimen (diameter about 2<sup>mm</sup>), having 48 unequal tentacles and 4 simple, elongated, marginal fronds. Duerden identified with it a small form of Lebrunia, having duchotomous fronds and agreeing nearly in color, etc., with L. Danæ. The identity of his specimens with the true Hoplophoria seems to me very doubtful. This generic name is unfortunate for its variants, Hoplophorus and Hopliphorus, have been used previously for five distinct genera. It evidently cannot be the young of either nominal species of Actinodactylus, for although much smaller, it has more tentacles. It is most likely to be the young of Diplactis Bernudensis McMur, or some similar species.

his description it is stated that they "dichotomize many times until a dendritic structure is produced." The rounded bodies are not figured nor described by him, nor by D. and M. as occurring on the fronds. In this respect the fronds are very different from those of the Bermuda species studied by me. I am, therefore, disposed to believe that there are two large West Indian species.

# Subfamily ALICINE = Family ALICIADE Duerden.

Duerden, Ann. and Mag. Nat. Hist., 6, xv, p. 213, 1895; Haddon and Duerden, Sci. Trans. Roy. Dublin Soc., vi, p. 153, 1896.

This family was established to include certain tuberculated genera, such as Alicia (= Cladactis Panc.), Cystiactis, etc.

It is characterized by a thin wall; feeble, diffused sphincter muscle; hollow tubercles, usually compound, on the column; 12, 24, or more pairs of perfect mesenteries; no acontia.

The wall-tubercles are thin and doubtless serve as branchiæ; they are not adhesive suckers.

The group is practically equivalent to tuberculated Actinidae, and might well form a subfamily of that family.

#### Eucladactis Ver., new name. Type, E. grandis V.

Cladactis Ver., Trans. Conn. Acad. Sci., i, p. 472, 1869 (non Panceri, 1868).

By a mere coincidence the name *Cladactis* was given by M. Panceri and myself to two distinct genera, at nearly the same time. The former appears to be the same as Alicia Johns. which preceded it. No other name seems to have been given, as yet, to my Cladactis. The latter is characterized by very numerous tentacles, which are scarcely retractile; column thickly covered with hollow clavate and lobulated tubercles, the upper ones larger and more lobed than the rest; margin with a deep fosse; sphincter muscle very feeble and diffuse, or almost lacking; 36, 48, or more pairs of perfect and many imperfect mesenteries, having feeble muscles extending along most of their breadth; gonads numerous, borne on most of the mesenteries, both perfect and imperfect; a distal septal foramen; mouth large, with two large equal siphonoglyphs; lips with very numerous lateral furrows.

## Eucladactis grandis Ver. Figures 13, 14.

Cladactis grandis Ver., Trans. Conn. Acad. Sci., i, p. 473, 1867. Andres, op. cit., p. 226, 1884.

The larger specimens of this species are over 2 inches in diameter and height, as preserved in alcohol. The tentacles

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are partially contracted in length and sulcated, but are rarely concealed, even in the young, by the infolding of the margin of the disk; generally they are fully exposed and the margin is but little contracted or not at all, owing to the feeble development of the circular muscles. There are about 480 tentacles in the larger specimens; they form five or six crowded rows. the inner ones standing about half way between the center and the margin of the disk; the inner ones are larger and somewhat swollen at the bases but are not much longer than the outer ones; all are sulcated by contraction. The lips have about 48 to 60 furrows on each side. The mesenteries are hexamerous and, like the tentacles, vary in number according to the age. A medium-sized specimen had about 120 pairs, of which about 48 were perfect, but the arrangement is more or less irregular, for one, two, or even three imperfect pairs may intervene between the various perfect pairs. The larger specimens have about 60 pairs perfect and about 180 imperfect. Nearly all bear gonads. The larger upper actinobranchs (fig. 14 a, c, next the smooth fosse, are elongated, more or less clavate, the distal portion divided into four to six irregular rounded or obtuse lobules; those lower down become shorter and less lobulated, but nearly all are clavate or capitate, to the base, and most of them, in large specimens, are divided into two, three, or more lobules. They are thickly crowded over the whole surface, and in alcoholic specimens appear to be united together in horizontal series by thin folds of the wall (fig. 14b).

Panama; Paita, Peru; San Salvador.

#### Explanation of figures.

Fig. 7. Haloclava producta (St.). Type, natural size. Fig. 8. Anthopleura Dowii V. Side view of a tentacle, actinobranch, and two upper verrucæ. Enlarged.

Fig. 9. A similar view of the same organs of Anthopleura Stimpsoni V., from the type, enlarged.

Fig. 10. Asteractis Bradleyi V. Type, about natural size. Fig. 11. The same, side view of tentacles and actinobranchs.

The same, view of a portion of the disk, tentacles, pseudofronds, Fig. 12. enlarged.

Fig. 13. Eucladactis grandis Ver. Type, ½ natural size.

Fig. 14. The same; a, one tentacle and a single vertical row of actinobranchs; b, a group of actinobranchs or papillæ from the middle of the column; c, various forms of marginal actinobranchs.

Fig. 15. Lebrunia Danæ, one of the actinobranchs with acrorhagi,  $\frac{1}{2}$  natural size.

Figs. 8 to 15 are by A. H. Verrill. Fig. 7 is by Wm. Stimpson.

Erratum-In part I, p. 494, line 17, for W. E. Coe, read W. R. Coe.

ART. VII. — Mineralogical Notes: Analyses of Tysonite, Bastnäsite, Prosopite, Jeffersonite, Covellite, etc.; by W. F. HILLEBRAND.

In the following pages are given the results of several analyses of minerals made in the laboratory of the U. S. Geological Survey during the past few years. In the cases of tysonite and bastnäsite the results show that the formulas attributed to them are correct, which in the absence of fluorine determinations could not hitherto be affirmed. In the other cases the analyses are interesting only as affording additional data regarding rare minerals from new localities.

#### Tysonite and Bastnäsite.

These minerals formed a single fine specimen half as large as the fist, without crystal faces, from Cheyenne Mountain, near Pike's Peak, Colorado. The bastnäsite covered one side of the tysonite to the depth of an inch. The line of demarcation between the two minerals was sharp, but examination of their sections by Mr. H. W. Turner showed the tysonite to be permeated by stringers of bastnäsite along numerous cracks and that occasional grains of the latter were imbedded in the tysonite, which accounts for the CO, shown in the tysonite analysis. Attached to the tysonite at portions of its surface were other white and brownish alteration products derived from it, as shown by qualitative tests. The tysonite was evidently the remnant of a single large crystal, since, according to Mr. Turner, all parts had the same optical orientation. Mr. Turner further found the optical properties of both minerals, so far as determinable, to agree with those given in Dana's Mineralogy, and the index of refraction of the bastnäsite to be greater than that of the tysonite. He likewise noted in both minerals minute colored inclusions, indeterminable and very trifling in amount, and also in the tysonite "numerous minute angular cavities in which there is a liquid, often with gas bubble. Minute, clear, cuboidal crystals, apparently isometric, were also noted in some of these cavities."

The composition of the minerals was found to be as given by Allen and Comstock, with the exception that the ratios of cerium oxide to the oxides of the lanthanum group are not quite the same. The formulas are not thereby affected.

Cerium was separated from the lanthanum group oxides by two precipitations by potassium hydroxide followed by long introduction of chlorine. After recovery of the earths remaining in solution, they were again subjected to this treatment to be certain of having all the cerium. In one case a small portion was thus recovered. The cerium was most carefully examined for thorium and traces of what appeared to be thoria were found. The other earths were wholly precipitable by potassium sulphate with exception of traces of what may be oxides of the yttrium group. Approximate molecular weight determinations of the combined oxides of these two groups were made, and they show an appreciable difference, which may, however, be due to the uncertainty of the method. It may be mentioned that on ignition of the sulphates of these earths they acted like the old didymium in that they lost exactly two-thirds of their SO, on ignition over the full flame of the Bunsen burner, a fact which would seem to exclude the presence of lanthanum. Their solutions were pink and gave pronounced absorption spectra. The ignited oxides freed from. cerium were a dull dirty brown, which became nearly white on blasting and acquired a distinct bluish cast on ignition in hydrogen. No appreciable reduction in weight followed heating in hydrogen. The material saved is at the disposal of any one desiring to examine these earths spectroscopically.

Owing to the great difficulty in effecting complete decomposition of the minerals by sulphuric acid at a single treatment, the fluorine was obtained in condition for estimation by fusing with potassium carbonate after mixing with silica in the proportion of 0.6 gram mineral to 1 gram silica.

Fragments of tysonite when held in the blast gave a distinct crimson flame showing the lithium red line, but an alkali determination failed to reveal more than a trace of this element.

Of the bastnäsite very little pure material could be separated, and it was therefore impossible to place with certainty all the loss shown by the analysis, but a portion of it is to be charged to the oxides of the lanthanum group because of an accident.

Sp. grav. of the bastnäsite  $5 \cdot 12$  at  $27^{\circ}$  C. and of the tysonite  $6 \cdot 10$  at  $28^{\circ}$  C., which becomes  $6 \cdot 14$  when corrected for  $2 \cdot 65$  per cent of bastnäsite.

Analysis of Tysonite.	Analysis of Bastnäsite.
Ce.O	Ce.O. 37.71*
La group 39.31 <sup>†</sup>	La group
F 28.71†	F 7.83
CO	CO 20.03†
CaÖ 18	Fe. <sup>0</sup>
Fe.O	Na 0§ 18
$Na_{a}^{2}O_{8}^{3}$	H.O
2.0	2
112.03	102.34
Less O for F, 12.08	Less O for F 3.30
99.95	99.04
* 13 per cent ThO <sub>2</sub> ?	* Mean of 37.73 and 37.69; in-
4 At. w. 139.7 : includes	cludes '10 per cent ThO <sub>2</sub> ?
21 per cent soluble in K <sub>2</sub> SO <sub>4</sub> .	+ At. w. 141; includes 09 per
t Mean of 28.86 and 28.56.	cent soluble in K <sub>2</sub> SO <sub>4</sub> .
S With traces of K and Li.	t Mean of 19.94 and 20.11.
0	8 With traces of K and Li.

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Neglecting the three last constituents in each case, the ratios become for

Bastnäsite....  $R: F, CO_3 = 1:2.94$ Tysonite....  $R: F, CO_3 = 1:3.05$ 

which ratio for tysonite is not changed by allowing for admixed bastnäsite.

The above direct fluorine determinations fully establish the hitherto assumed formulas,  $R'''F_s'$  for tysonite and  $R'''(F,'CO_s'')$  for bastnäsite.

### Prosopite.

Over two years ago Mr. Geo. F. Kunz sent for examination a beautiful pale green mineral from Utah, supposed to be identical with the green variscite called by him utahlite in Mineral Resources of the U. S., 1894, p. 602. Under a recent date Mr. Kunz writes that Mr. T. H. Beck of Provo found the mineral "in 1895, in the Dugway mining district, Torvel Co. It was found in a low range of hills about five miles long, surrounded by a desert on an arid region occurring as flat rock, associated with fluorite, native silver and slate, and trachytic rock (?), containing decomposed pyrite in which there was present a little free gold."

Unexpectedly this was found to be the hydrous aluminumcalcium fluoride prosopite, mixed with some quartz and probably fluorite and colored by a small amount of some copper salt. A new and interesting occurrence for this very rare mineral is thus afforded.

The material as prepared for analysis after separation by a heavy solution proved to be still far from pure; quartz grains in amount from one to two per cent were left undissolved after complete conversion of the fluorides into sulphates and presumably considerably more had been removed by the escaping fluorine. The total amount of quartz was not determined and the material at hand did not suffice for attempts at more complete purification, so that the conclusions drawn from the analysis, while extremely probable, are not to be taken as altogether proven.

The sp. gr. of the mineral as analyzed was 2.87 at 21° C. and the hardness about 4.5, both agreeing with the constants for prosopite. Furthermore, but little of the water (1.25 per cent) was expelled by several hours heating at 280° C. Analysis gave :

Al	20.08
Ca	17.55
Mg	trace
К	•12
Na	$\cdot 32$
Cu	.17
F	28.00
Н.О	14.24
Quartz and oxygen	19.52

100.00

Neglecting copper, alkalies, and the oxygen calculated for their oxides, and assuming the water to exist entirely as hydroxyl, the following not very satisfactory atomic ratios result:

Al	.7407	2
Ca	•4380	1.18
F	1.4690)	0.00
Hydroxyl	1.5808	8.23
	,	

which become

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Al	.7407	2
Ca	$\cdot 3712$	1
F	1.3354)	5.05
Hydroxyl	1.5808 ∫	1.81

if enough calcium and its equivalent in fluorine are subtracted to make the ratio A1: Ca exactly 2: 1, on the not improbable assumption that fluorite is present as an admixture, an assumption that had to be made also for the Colorado prosopite in order to bring it into close agreement with Brandl's formula.

There is now a deficiency in the acidic radicals. The figures for Al, Ca, and  $H_2O$  are undoubtedly very nearly correct while the fluorine may well be half a per cent low, having been determined by the Berzelian method, owing to the difficulty of securing complete decomposition of the fine powder by a single treatment with sulphuric acid. Let it be permitted to balance the basic and acidic radicals by raising the fluorine, and to figure the ideal percentages on this basis. These become of interest when compared with the corresponding figures for prosopite from Altenberg and Pike's Peak as given below:

	Altenberg.	Pike's Peak.	Utah.
Al	23.37	22.02	22.74
Ca	16.19	17.28	16.85
F	35.01	33.18	29.95
H <sub>0</sub> O	12.41	13.46	16.12
0	12.58	13.41	14.34

100.00
If the assumptions made in the foregoing are justified, the Utah mineral is prosopite, and further evidence is afforded of the correctness of the view established by Penfield that fluorine and hydroxyl can mutually replace one another in many mineral species, for their relative proportions differ materially in the prosopite from the three known localities. The correctness of the formula as applied to the Colorado and Utah prosopite is, however, predicated, as said, on the unproven assumption that the material analyzed contains some admixed fluorite.

#### Jeffersonite.

Two brown substances associated with franklinite and other zinc minerals from Franklin Furnace, N. J., so alike in appearance as to have been taken for the same mineral species, were received from Mr. Geo. L. English. One was a little duller than the other and proved to be a mixture of several minerals according to Mr. F. L. Ransome of the Geological Survey, largely pseudomorphic after some micaceous mineral. From Prof. Clarke's calculations, based on the following analysis, it might be a mixture of a calcium-aluminum garnet, troostite, and limonite. SiO<sub>2</sub> 32·09, Al<sub>2</sub>O<sub>3</sub> 11·12, Fe<sub>2</sub>O<sub>3</sub> 5·16, MnO 15·85, ZnO 16·89, CaO 15·65, H<sub>2</sub>O 2·15, MgO and alk 1·12; total 100·00.

The other was of a richer and deeper brown and showed such a pronounced cleavage or parting in one direction as to produce a lamellar structure. The luster was brilliant on these cleavage surfaces. Other directions of cleavage were apparent. The hardness was about 5.5 and the density 3.39 at 21.5° C. Before the blowpipe a fragment fused with difficulty to a light colored blebby glass. Analysis gave:

SiO,	51.70
Al <sub>s</sub> Õ <sub>s</sub>	•36
Fe O	.37
MnO <sup>°</sup>	7.43
ZnO	3.31
CaO	23.68
MgO	12.57
Na O	.12
K.Ö	trace
НО	.65
	100.10

TiO<sub>2</sub>, FeO, P<sub>2</sub>O<sub>5</sub> absent.

Neglecting the sesquioxides, alkalies and water, this leads to the ratio  $SiO_4: RO = 1:1.02$ , and the formula is that of a metasilicate R'/SiO<sub>4</sub>. According to Mr. English the material submitted by him had been pronounced by Prof. Penfield on the basis of qualitative tests to be jeffersonite, a manganesezinc pyroxene, a statement supported by the analysis above given, although neither the color of the mineral nor its quantitative composition agree with the hitherto published data. In Dana's Mineralogy the color is given as "greenish black, on the exposed surface chocolate brown," the density as 3.36 on p. 358, but 3.63 on p. 360. The discoverers of the species, Keating and Vanuxem, give 3.50-3.55 for the density and 4.5 for the hardness. The present mineral presents all the evidences of being fresh and unaltered, yet it is brown throughout, and its analysis furnishes figures widely at variance with those of Herrmann and of Pisani, but giving a better metasilicate ratio than either of their analyses. Notwithstanding these discrepancies, there is no reason for ascribing to the mineral a new sub species name. The analysis is chiefly valuable as showing a wide range of composition for the mineral.

#### Covellite, Enargite, Stalactite.

The only important occurrence of covellite in this country is at Butte, Montana, where it occurs in splendid indigo-blue masses. Specimens from the East Greyrock mine, collected by Mr. Geo. W. Tower of the Geological Survey, gave almost the theoretical composition as shown below. Sp. gr. at 26° C. 4.76, uncorrected for impurities.

An analysis of enargite collected by Mr. Tower in the Rarus mine, and of a beautiful sky-blue stalactite from the Anaconda mine, both at Butte, are likewise given.

Covellite.	Enargite.	Stalactite.
Cu 66.06	Cu 48.67	CuO 9.32
S 33.87	Fe 33	FeO18
$Fe \dots \cdot 14 = \cdot 30 FeS_2$	Zn •10	MgO •08
Insol. '11	As 17.91	Al <sub>2</sub> O <sub>3</sub> 10.67
	Sb 1.76	SO, 35.05
100.18	S 31.44	$P_2O_5 = 1.13$
Ratio Cu: S as 1:1.01	Insol ·11	As <sub>2</sub> O <sub>5</sub> 07
		H.O 43.44
	100.32	Insol '06
		100.00

The stalactite was of some size, and was most readily soluble in cold water, the solution giving a strong acid reaction. The calculated ratio is strongly acid, showing either a mixture of highly acid salts or of normal salts with free acids.

#### Fibrous sulphate.

Mr. W. H. Weed collected in the St. Paul mine, near Whitehall, Montana, a magnificent specimen of a compact soluble fibrous sulphate, supposed to be melanterite. It seemed to be a filling between fragments of broken rock. Outwardly it was white from dehydration, but at some depth the unaltered green mineral was to be found. This had the following composition:

4.34
9.04
.03
2.62
1.06
•05
.09
3.07
.07 ?
29.88
none
48.84
•16
99.25

Of the water 10 per cent escaped in 24 hours over sulphuric acid and only  $\cdot$ 4 per cent more in another like period, but a total of 14 $\cdot$ 4 per cent after 10 days uninterrupted exposure. The water thus lost is very slightly reabsorbed on exposure to air.

From calculations by Prof. F. W. Clarke the substance may be regarded as a mixture of alunogen or the halotrichite group with salts of the melanterite group, the empirical formula being nearly

 $(Fe, Mn)_4(Zn, Mg)_2Al_2(SO_4)_2 \cdot 65H_2O.$ 

The outer white zone of the specimen contained only 39.62 per cent of water.

Laboratory of the U. S. Geological Survey, July.

## ART. VIII. -- What is the Loess? by F. W. SARDESON.

THERE is wide difference of opinion regarding the origin of the American loess. Is it an aqueous or an æolian deposit? Many believe it to be partly aqueous, partly æolian, and thereby raise the very important question of how to distinguish the one kind of loess from the other. To those who view the loess as æolian, this discrimination is easy, for the loess is all æolian except locally where distinct sedimentary characters appear. The loess is interpreted by them as wind-carried dust, deposited on a land surface interrupted by streams and ponds.

The loess viewed as a sediment is also easily distinguishable from other sediments, but requires then the very difficult explanation of how a little altered glacial sediment could be so peculiar,--in fact like dust deposit. Negative evidence to this theory is found in a region like Minnesota, where there are thousands of existing and extinct lakes of glacial origin, in not one of which is loess known to have deposited,-not even in They have in them gravels, sand and silt, and Lake Agassiz. around them are beaches. No small nor shallow lake could have spread over the extremes of altitude on which the loess lies, and a necessarily huge body of water must have left some beaches and coarse sediments besides silt or loess. It was not a lake that deposited the loess. The loess could also scarcely be all a glacial sheet flood deposit. For example, the Iowan loess lies beyond the Iowan drift sheet as it were its continuation. Either the loess is the older and hence remains intact only beyond the Iowan glacier's domain, or else the loess is contemporaneous and deposited by agency of the same glacier's waters. The latter is the sedimentary theory. But the theory does not explain why the glacial waters ceased depositing loess when the glacial retreat began. Iowan loess does not cover the Iowan drift,\* and this fact the æolian theory alone can explain. Partial or entire recognition of the æolian origin is necessary.

Partial recognition does not, however, remove all inconsistencies, because "no means of discriminating between the two kinds of loess are yet known to be formulated,"+ as the advocates of the mixed hypothesis<sup>‡</sup> say. Prof. T. C. Chamberlin teaches this double origin of the loess, and his view, as understood by the writer, is that the glacial waters flooded

<sup>\*</sup> Prof. S. Calvin discredits the reported slight occurrence of this loess on the Iowan drift. Iowa Geol. Sur., vol. viii, p. 174; see also p. 339. † C. R. Keyes, this Journal, vol. vi, p. 229. ‡ T. C. Chamberlin, Jour. Geol., vol. v, p. 795.

sediments upon the land, and these were in part modified by æolian agent into "bluff loess."

In theory, the Chamberlin view may be essentially correct. The loess particles came from the drift, and very probably from washed drift largely. If the theory be applied, it should bring into recognition the following kinds and relations of deposits: the unassorted glacial deposit, or till; this, when assorted by agency of water, becomes stratified gravel, sand and silt; the two latter may be made by æolian agent into dune sand and "bluff" loess; and they, after erosion, may become again respectively stratified sand and silt; under the action of humic acids the silt of both kinds may be reduced to a loam in which there is no lime; and likewise the "bluff" loess may be reduced entirely, or to a degree, to "loess" loam. The till is easily recognized, as are also the stratified products, the gravels and sands. Dune sand lacks the assorted and strati-fied structure, and is easily distinguishable from the sedimentary patches associated with or in it. It seems strange, therefore, that silt and æolian deposit,-that is mud and dust,should not be distinguishable.

Indeed, it is not difficult to discriminate between glacial silt and loess, and I believe that they are rarely if ever confused by geologists. The difficulty lies in the discrimination of theoretical sedimentary loess and æolian loess. There are two kinds of loess in the Mississippi basin, and they are distinguishable at a glance, but as said, they have not been proved separable on the basis of sedimentary and æolian origin. The two kinds are very intimately associated. They are respectively the characteristic calcareous, porous, "bluff" loess and the oxidized portion of the same, which may be called loess loam, residuary loess, or ferretto. Difference in color, or the appli-cation of hydrochloric acid, serves as a ready test of them.\* Chamberlin and Salisbury, in their monograph, recognized the loess loam of the "Driftless Area" as residuary clay although they failed to connect it with the loess, as I have once before indicated, + and in fact Chamberlin has practically admitted the emendation by criticising other parts only of my paper.<sup>‡</sup> The loess loam being due to oxidation by humic acids, its depth is determined by the vegetation upon its surface and by the time that this agent has acted, provided that the loess be not too shallow and surface erosion does not equal or exceed the rate of oxidation. On the Missouri and Mississippi River bluffs, the loess was originally deepest; it is also little covered with vegetation and highly exposed to erosion. On the higher

\*This distinction is not new, for example see Geologischer Fuchrer d. Umgebung v. Freiburg, p. 78, Steinmann u. Graeff, 1890. † Am. Geol., vol. xx, No. 6. ‡ Jour.

<sup>‡</sup>Jour. Geol., vol. v, No. 6.

but more level land farther from the great rivers, the loess was thinner and was also more oxidized. Often it is all oxidized.

From my own observations compared with published descriptions, I feel safe in saying that, as a rule, the loess loam is what has been called sedimentary loess. If it *were* such, why is it not calcareous as are the known glacial silts? And if the "bluff" loess is derived from it, why is the former calcareous, since the latter is not? There is no explanation.

The above criticism applies to the loess as a rock type, but when the Loess formation is considered another distinction should be admitted, namely that there are two distinct loess formations, as H. F. Bain describes in northwestern Iowa,\* which are comparable to the older and younger loess of the Rhine Valley. Each may bear loam.

The loess as a formation bears loam both upon and within. Upon the loess, the loam represents the portion which has been oxidized since the loess formation was deposited, while in the same it indicates patches of vegetation that were contemporaneous with the deposition. The loess loam, in combination with land and fresh water shells, forms the very strong argument in favor of the purely æolian origin of the loess. The æolian hypothesis is the one which permits the several parts of the loess to be both readily interpreted and easily recognized in the field, and it has therefore a distinct advantage over the semi-æolian hypothesis. It is further competent to explain without inconsistency the dune sands on the river bluffs and their graduation into the loess; wind polished pebbles lying between till and loess are recognized; two kinds of stratified silts existing with the loess or graduating into it are identified as respectively glacial silt from which the loess seems to have been largely derived, and modified or washed loess. Banded structure in the loess, + which is not true stratification, indicates the line of a moist zone where vegetation thrived and oxidized the loess. Dry runs and very probably rodent burrows and mounds can be easily recognized; and the occurrence of land and fresh water shells is not anomalous. Finally, when it is observed that much loess accumulated before one glacial period or ice advance and little before another, the same is consistently attributed to climatic conditions, to which kind of cause the glaciers themselves are referred.

University of Minnesota, Minneapolis.

\* Iowa Geol. Sur., vol. viii, p. 240.

+ See for example, fig. 32, p. 235, vol. vii, Iowa Geol. Sur.

#### ART. IX.—Absorption of Gases in a High Vacuum; by C. C. HUTCHINS.

THE term "absorption" is here used to cover the general phenomenon of the disappearance of the residual gas in a high vacuum under the electric discharge, whatever may be the cause of the disappearance.

It is well known to all users of X-ray apparatus that under the discharge from an induction coil the tubes rapidly rise in vacuum, and the current, after a longer or shorter time, ceases to pass, and the usefulness of the tube is at an end. This rise in vacuum constitutes the most serious defect in such tubes and is a source of constant annoyance.

It is probably safe to reject the theory that the electromotive force drives the molecules of the residual gas through the walls of the glass. It is possible to have an opening into a highly exhausted tube without the entrance of air.

This laboratory has for twenty years possessed a Crookes radiometer that has during all that time been cracked entirely around near the top of the bulb, but which, notwithstanding, continues to function perfectly. We also had for several months an X-ray tube similarly cracked. By constant use this tube became so high in vacuum that it was punctured by a spark; air entered and the cracked end fell away of its own weight.

The disappearance of the gas is therefore probably due to mechanical and chemical combination with the metallic electrodes of the tube, and it should be possible to find some gas or vapor whose rate of absorption would be less in rate or extent than that which takes place in the ordinary tubes.

The first step in the inquiry is to learn what the ordinary high-vacuum tube contains.

If a Plücker tube, made from carefully cleaned glass, be very highly exhausted and then the current from an induction coil turned into it, the vacuum falls at once, air and water being driven from the walls of the tube. If now by heating the tube, continuing the current and working the pump, the vacuum be again raised to the point at which the fluorescence of the glass appears, the spectrum of the tube will be found to consist of the red and blue lines of hydrogen (C and F), and three or four lines of oxygen; that is, the tube contains only water. The tenacity with which glass retains water upon its surface is well known; and it is necessary to heat the glass nearly to its softening point before the last of the water comes away. When the vacuum in a tube is so high that the current will not pass, heating the tube will dislodge a little water and the current will pass until the water has again condensed upon the cooling of the tube.

As the following experiments had for their object the production of a permanent state of vacuum under the electric discharge, they were limited to such gases as could be produced readily in the tubes themselves, and whose use seemed to hold out promise of success.

A number of Plücker tubes were made, as nearly alike as possible, and each provided with a small communicating tube containing some chemical that would yield the desired gas by the application of heat. The chemicals were prepared as pure as possible, and dried at a hundred degrees for twenty-four hours. The dried-out tubes, containing the chemicals, were then attached to the mercury pump and exhausted; heated very hot and pumped to remove all water vapor. The tube containing the chemical was then heated, gas driven off into the tube and the exhaustion repeated.

In nearly every case it was found impossible to entirely get rid of water vapor, even by repeatedly washing out with the gas. The tubes were sealed at such a degree of exhaustion as would allow the subsequent rise in vacuum to be well marked, when the green fluorescence of the glass appeared at the cathode, and the sparking distance across the terminals of the coil and in parallel with the tube was  $2^{mm}$ . After the tube was sealed, it was placed before a spectroscope, and the current from the coil passed until the spectroscope showed the entire absorption of the gas, or until the vacuum became too high for the current to pass readily. A fairly good idea of the relative rates of absorption of the various gases may be obtained from the time required for the absorption to take place.

Tube containing zinc cyanide. This substance yields cyanogen when heated. The tube was washed out with the gas as above described and sealed. The vacuum began to rise at once as soon as the current was turned on. In five minutes the whole tube became fluorescent, and in seven minutes the cyanogen was entirely absorbed, the spectrum being now that of the trace of water vapor from which the zinc cyanide could not be freed. It is difficult to see why a gas which if decomposed by the discharge would remain as the chemically inert nitrogen, should disappear at such an extraordinary rate. To test the matter further another tube was made in such form that when the vacuum became higher than a certain value, a portion of the current was shunted through a platinum wire surrounded by zinc cyanide, and so the vacuum was automatically maintained nearly constant. This tube was worked for four hours, and the yield and absorption of the gas went on for the whole time at a nearly constant rate.

Tube containing lead ferrocyanide, yielding nitrogen when heated, also gave considerable water vapor. Sealed at a slightly lower vacuum than the first, yet the nitrogen all

### Hutchins-Absorption of Gases in a High Vacuum. 63

vanished in ten minutes, water alone remaining. As it was possible in these two cases that the gases had undergone reabsorption upon the cooling of the substances from which they had been expelled, a fresh portion of the gases was driven off and the tubes allowed to stand twenty-hours. No change could be observed in them.

Tube containing iodine.—The iodine was shut off from the main tube by a stopcock, fearing its vapor tension at ordinary temperatures would be too great to admit of obtaining a sufficiently high vacuum. The tube was exhausted, the stopcock opened for a moment to fill the tube with iodine vapor, and the exhaustion repeated. After sealing, the iodine disappeared under the action of the current in less than a minute. The tube was filled with iodine vapor again by opening the stopcock and warming the tube. Upon again starting the current the platinum mirror upon the glass at the cathode was seen to be attacked and converted into a dark bronze-colored substance and the iodine again disappeared.

Tube containing oxide of mercury, yielding oxygen when heated, but no water vapor. Tube pumped and heated very thoroughly, and when sealed showed the spectrum of oxygen and the red hydrogen line faintly. The vacuum rose slowly; after fifteen minutes the hydrogen line disappeared; at the end of an hour the vacuum had become quite high, the spark in parallel with the tube being two inches, but the current still passing easily. The spectrum of the tube then consisted of three lines of oxygen.

Experiments were also made with carbon dioxide and some other gases, the details of which need not be given here, inasmuch as it was found that oxygen was absorbed far more slowly than any other substance tried. Mercury oxide is also eminently adapted to maintaining a condition of constant vacuum. It yields oxygen only at a high temperature, and the flow of gas ceases immediately upon withdrawal of the source of heat.

To construct an X-ray tube in which the vacuum may be maintained at the most efficient point, it is only necessary to attach near the anode terminal a short tube having a sealed-in platinum wire packed around with oxide of mercury. A plug of asbestos may be used to hold the substance in place. When by use the vacuum becomes too high, a portion of the current is shunted from the cathode through the oxide of mercury for a brief time; a little gas is dislodged and the tube becomes as new. The shunt may be left permanently in place with a longer or shorter spark-gap at the mercury terminal. The action will then be automatic, and vacuum remain indefinitely at any desired point.

Searles Physical Laboratory, Bowdoin College, November, 1898.

#### SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. On the Extraction of Nickel by the Mond Process .- A paper by ROBERTS-AUSTEN has recently appeared giving an account of the application of the volatile nickel-carbonyl, discovered by Mond, to the extraction of nickel from its ores. Mond's discovery was that metallic nickel forms a volatile compound with carbon monoxide, which he called nickel-carbonyl, which boils at 150° and from which the nickel may again be regenerated by heating to 180°. Iron, while not as active, acts similarly. The suggestion was an obvious one, that by means of these volatile compounds, these metals might be separated from cobalt, copper and the others with which they are associated in their ores. An experimental plant was erected in 1892 near Birmingham. The material used was Bessemerized matte, which after roasting contained 35 per cent nickel, 42 per cent copper and about 2 per cent of iron. By treatment with sulphuric acid, about two-fifths of the copper was removed, the residue containing 51 per cent of nickel. The remaining copper was reduced to the metallic state by means of water gas at 300°. The ore was then treated in a volatilizing tower with carbon monoxide, the temperature being kept below 100°. The volatile nickel carbonyl passed to a decomposer-a horizontal retort heated to 180°-where the nickel was released in the metallic form and the carbon monoxide returned to the volatilizer to be again used. The unused metallic residue was returned to the roasting furnace. The nickel produced was 99.8 per cent pure. Up to the time Professor Roberts-Austen visited the plant, about 80 tons of nickel had been thus prepared, with quite satisfactory results.-Nature, lix, 63, November, 1898. G. F. B.

2. On Ætherion.\*—A note on ætherion has been published by CROOKES, giving some of his old researches made from 1873 to 1881, tending to show that the new gas may be nothing more than aqueous vapor. Early in his investigations he noticed that a little aqueous vapor thrown into the vacuum [of a radiometer], converted into attraction the repulsion due to radiation. In 1880, he observed that aqueous vapor was found to retard the force of repulsion to a great extent and carbonic acid acted in a similar way, though less in degree. "The presence of even a trace of aqueous vapor was found to have a strong action in diminishing the sensitiveness of the radiometer and other instruments," he says. As to the absorption of ætherion by glass and its evolution again on heating, the author gives an experiment made in 1879 showing that air-dry glass condenses on its surface a considerable quantity of water and carbonic acid which does not come off

\* This Journal, IV, vi, 431, November, 1898.

until heat is applied. As to its conductivity for heat, experiments are described which show that at high vacua water gas is a better conductor than either air or hydrogen at similar pressures. "It has been found," he says, "that as water gas is rarefied, its heat conductivity diminishes in a greater ratio than that of hydrogen." "At these high vacua water gas gains so rapidly on hydrogen that I am prepared to believe that at Mr. Brush's low pressure of 0.38 millionth, the ratio may even be as great as that he ascribes to etherion." "On the evidence at present available," he concludes, "I consider it more probable that ætherion is water vapor than that it is a new elementary gas."—*Chemical News*, lxxviii, 221, November, 1898. G. F. B.

3. On the Preparation of Graphitic Acid.-An easy method of preparing graphitic acid has been described by STAUDENMAIER. A mixture is first made of 100°° of concentrated nitric acid (sp. gr. 1.4) and 300<sup>cc</sup> of ordinary strong sulphuric acid. To this are added 50 grams of pulverized Ceylon graphite, and then 100 grams of potassium chlorate, in small portions at a time; the whole being frequently stirred. After the mixture has stood for several hours, it is poured into water, and the solid is washed, dried and ignited in a large dish of metal until it has intumesced. Then it is again stirred with water, and the portion that floats is collected for use in the subsequent operations. Of this prepared graphite, 25 grams are poured, with constant stirring, into a cold mixture of one liter of strong sulphuric acid and half a liter of strong nitric acid contained in a shallow dish, and then about 450 grams of potassium chlorate are added in successive portions. After the active evolution of gas diminishes, and a sample of the resulting green substance appears pure yellow on treating it with acid permanganate, the whole is poured into water, and the resulting solid is washed repeatedly by decantation. It is now placed in a dish and a solution is added to it consisting of seven grams of potassium permanganate dissolved in 120<sup>cc</sup> of hot water; after cooling, a mixture of 15<sup>cc</sup> of strong sulphuric acid with 75<sup>cc</sup> of water is added, and the whole is heated on the water bath until the red color has disappeared. Hydrogen peroxide is added, the whole is allowed to stand at rest for some time with occasional stirring, and the graphitic acid is then washed first with dilute nitric acid and finally with alcohol and ether .- Ber. Berl. Chem. Ges., xxxi, 1481-7, June, 1898. G. F. B.

4. On Compounds of Lithium and Calcium with Ammonium. —The fact has been observed by MoISSAN that when liquefied ammonia, contained in a tube cooled to  $-50^\circ$ , is brought in contact with metallic calcium or lithium, solution takes place with the production of an intense blue liquid having a brown red reflection; this result being comparable to the similar phenomenon observed with potassium and sodium. These latter metallic ammoniums when thus produced, according to Joannis, have the formulas KNH<sub>3</sub> and NaNH<sub>3</sub>, and they decompose at the ordinary temperature and pressure, evolving ammonia gas and regenerating

AM. JOUR. SCI.-FOURTH SERIES, VOL. VII, NO. 37.-JANUARY, 1899.

the alkali metal in brilliant crystals, as Seely long ago pointed out. As opinions differ as to whether these metallic ammoniums are molecular or atomic in constitution, the author has made experiments with potassium, sodium, lithium and calcium. Each metal was placed in a U-tube of glass, one leg of which was drawn out fine, while the other was recurved and connected with a source of ammonia gas, dried first over fused potassium hydrate and then over sodium. The four tubes were united successively so that the same current of ammonia gas traversed them all. By the use of a water bath, the temperature could be regulated, and the flow of gas increased or diminished by means of a tap. For low temperatures acetone was used in the bath, being cooled even as low as -75°, the solidifying point of ammonia, by adding to it fragments of solid carbon dioxide. The experiments were made under atmospheric pressure. It was found that lithium was attacked at  $+70^{\circ}$  with liquefaction, calcium at  $+20^{\circ}$  without liquefaction, potassium at  $-2^{\circ}$  with liquefaction, and sodium at 20° with liquefaction. It is clear therefore that these four metals unite directly with ammonia gas, the temperatures obtained being the superior limits of the action and at the same time the decomposition-temperatures of the metallic ammoniums under the conditions. By preparing the metallic ammonium by the action of the liquefied gas, and then slowly raising the temperature, the inverse method was effected, the sodammonium dissociating at -20° and giving the metal and ammonia gas, and the potassammonium doing the same at  $-2^{\circ}$ ; while calcium-ammonium and lithium-ammonium were stable at the ordinary temperature and pressure. Moreover, ammonia gas solidified at -80°, does not attack either of the four metals, though action takes place as soon as liquefaction commences with evolution of heat. If the experiment is made slowly, the author states that amides of these metals are produced; while when it is rapid, the metallic ammonium may be readily produced at the ordinary pressure and the metal regenerated in crystals without the production of amides. Lithium placed in a U-tube at the temperature of the laboratory and subjected to a current of ammonia gas, takes a brownish-red tint and liquefies, producing a liquid of the same color. Heated rapidly to +70°, the excess of ammonia escapes, leaving a reddishbrown solid, which takes fire in contact with the air. If lithium be placed in liquefied ammonia, the tube being allowed to return slowly to the ordinary temperature, the dark blue liquid becomes thicker, reaching a sensibly constant composition after 24 hours. The composition then was found to be : NH, 89.04, 87.00, 88.72, and 88.37 in four samples; the formula (NH.) Li requiring 87.93. The liquid may therefore be considered either as a saturated solution in ammonia gas or as a compound NH<sub>s</sub>Li.(NH<sub>s</sub>)<sub>2</sub>. As to solid lithium-ammonium, its composition was determined (1) by weighing the ammonia fixed by the metal and (2) by preparing the com-pound and determining the ammonia in it. The lithium found in five experiments was 28.07, 28.40, 28.72 and 28.82 per cent.; the

ammonia being 71.93, 71.60, 71.28 and 71.18. Theory requires for NH Li, 29.16 of lithium and 70.83 of ammonia. It is much less soluble in liquid ammonia than the sodium compound. The metal calcium exposed at 15° to a current of ammonia gas takes a yellowish-brown tint, becomes heated and increases in volume. At a temperature between 15° and 20° only a solid compound is formed, which takes fire in contact with the air and which fixes liquid ammonia and becomes pasty, being then soluble in the liquid. Like lithium, it gradually decomposes at the ordinary temperature, yielding transparent crystals of amide  $(NH_a)_2$ Ca and evolving hydrogen. On analysis calcium-ammonium gives numbers agreeing with the formula  $(NH_a)_4$ Ca.—C. R., cxxvii, 685–692, November, 1898.

5. On the Spectra of Iodine.-The results of a measurement of the lines in the emission and absorption spectra of iodine from wave-length 3030.5 to wave-length 6191, expressed in Angström units, have been given by KONEN. As is well known, either a line spectrum or a band spectrum can be obtained in a vacuum tube. The latter is composed of two different portions which may be designated as  $B_R$  and  $B_V$ ; the former of these,  $B_R$ , is identical with the absorption band spectrum, while  $B_v$  is not. When the discharge is very intense, however,  $B_n$  disappears, while  $B_v$ increases in intensity; so that the author is inclined to the view that  $B_{\rm R}$  is due to the ordinary iodine molecules, and  $B_{\rm v}$  results from dissociation. In the line spectrum also, two series may be distinguished, but it is quite possible that in this case the second series may be produced by an impurity. Tables of the wave lengths are given in the paper.-Ann. Phys. Chem., II, lxv, 257-286, 1898. G. F. B.

6. A Manual of Chemical Analysis, Qualitative and Quantitative; by G. S. NEWTH, Demonstrator in the Royal College of Science, London ; 8vo, pp. xii, 462. New York, 1898 (Longmans, Green and Co.).-The author tells us in the preface to his book that he has "done his best to make it as little of a cram-book as possible, but has endeavored to teach analytical chemistry as well as analysis-that is, the theoretical as well as the practical side of the subject." Book I treats of Qualitative, Book II of Quantitative Analysis. The quantitative work is divided into gravimetric methods, including electrolysis, and volumetric methods, including gas analysis; special methods following these. The great convenience of having the leading facts well set forth in a work of moderate size, for the use of students taking short courses, is well exemplified in this manual. The portion on volumetric work seems especially good. G. F. B.

7. Stratified Brush Discharges in Atmospheric Air.-M. TOEPLER has described a species of stratification in brush discharges (Wied. Ann., lxiii, p. 109, 1897) and the present paper is a continuation of his studies in this direction. A sixty-plate Toepler-Holtz machine was employed, and it was found that the increase of potential-difference was closely proportional to the increase of sparking distance; and that the potential difference at the electrode is nearly independent of the current strength if the discharge is of the nature of a brush. The G. Wiedemann-Hittorf law for Geissler tube discharges therefore holds also for brush discharges in free air.— Wied. Ann., No. 12, 1898, 660-675.

The writer has substantiated the results of Toepler, as far as relates to the stratification, by the employment of an apparatus which can produce a difference of potential of three million volts. The stratification with this high voltage occurs in the neighborhood of the positive pole.

8. The Spectrum of Lightning.—Photographs of the light of a spark six feet in length, taken in the Jefferson Physical Laboratory, show atmospheric lines very strongly developed between E and H. No more lines were produced by a voltage of three million than can be brought out with a voltage of one hundred thousand. With the higher voltage, however, there is a complete absence of the metallic lines of the terminals. The photographs taken with the high voltage therefore must closely resemble the spectrum of lightning.

9. Dispersion in the Electrical Spectrum.-Observations on dielectric constants for periods between wave lengths 2cm to 75cm have hitherto been wanting. E. MARX has endeavored to supply this break in the subject and has applied to his results certain laws of dispersion. He speedily ascertained that in order to obtain very short electrical waves it is necessary to so interlock the primary and secondary circuits, or in other words the exciting and reso-· nating circuits, in such a manner that only the fundamental vibrations of the primary circuit were in evidence. He employed Drude's method of measurement, which consists in nodes measureing the displacement of the electrical waves on wires, when a portion of these wires are surrounded by a dielectric. By means of an exciter of small dimensions he obtained electrical waves. 4cm, 36cm, and 58cm in length. The positions of the nodes were ascertained by means of a Zehnder-Geissler tube. The index of refraction of electric waves, 3.2cm in length, for water was found to be

$$n^2 = 85.0 \text{ (at } 17^\circ \text{ C.)}$$

For wave length 36<sup>cm</sup>

$$n^2 = 82.50$$
 (at 17° C.)

For wave length 53<sup>cm</sup>

$$n^2 = 83.73$$
 (at 17° C.)

The indices of refraction of ethyl-alcohol were similarly investigated. It was surmised that absorption bands of great extent in the ultra-red modify existing dispersion formulæ. A difference in concentration of the ethyl-alcohol solutions of 1 per cent can change the square of the electrical index of refraction 35 per cent. -Wied. Ann., No. 11, 1898, pp. 411-434; ibid., No. 12, 1898, pp. 597-622. J. T.

10. Traité Élémentaire de Méchanique Chimique fondée sur la Thermodynamique par P. DUHEM. Tome iii, Les Melanges homogènes; les dissolutions, pp. 1-380. Paris, 1898 (Librairie Scientifique A. Hermann).—The third volume of the extensive work by M. Duhem, which was announced in volume iii, p. 419, of this Journal, has now been issued. It shows that the promises made at the outset are being thoroughly fulfilled, and that the work when completed will occupy a unique place in scientific literature.

The volume is divided into two parts; the first of these discusses homogeneous mixtures with respect to thermodynamic potential, osmotic pressure and the hypotheses of Van t'Hoff and d'Arrhenius; also chemical reactions in homogeneous systems. The second is devoted to solutions, discussing the solution of salts in general, the effect of vaporization of the solvent, with the formulas of Kirchhoff, the effect of freezing of the solvent, saline and gaseous hydrates, and double salts. This enumeration of the subjects of leading chapters will serve to show the scope of this part of M. Duhem's work, but only close study will make the reader familiar with the thoroughness of the discussion as a whole.

11. Prismatic and Diffraction Spectra. Memoirs of Joseph von Fraunhofer. Translated and edited by J. S. AMES.—The inauguration of the series of Harper's Scientific Memoirs was announced in the last number of this Journal (p. 504, Dec., 1898). The second volume has now been issued; it contains translations of Fraunhofer's classical papers (1817–1828). To these are added the note by Wollaston (1802) describing the method by which he obtained a pure solar spectrum and discovered the presence of fixed lines in it. This volume, like its predecessor, is edited by Prof. Ames.

### II. GEOLOGY AND MINERALOGY.

1. Maryland Geological Survey; WILLIAM B. CLARK, State Geologist. Vol. i, pp. 1-539, plates i-xvii, 1897; Vol. ii, pp. 1-509, plates i-xlviii, figures 1-34, 1898,-Maryland was one of the first four states in the Union to institute an official geological survey, and, in the present series, is preparing the most elaborate and elegant geological reports that any state has so far produced. This second official survey of the state was organized by act of the General Assembly in March, 1896. The commission appointed Prof. Wm. B. Clark state geologist, and the two volumes are the work of the first and second years of the survey. The first volume, as the geologist says in the preface, "consists primarily of a summary of past and present knowledge concerning the physical features of Maryland, and embraces an account of the geology, physiography and natural resources of the state. The "Historical sketch," comprising Part ii, begins with the landing of Captain John Smith, in 1608, and narrates the work of the successive explorers and investigators who have developed the knowledge of the resources of the state. Part iv, on the Bibliography and Cartography, is compiled by Mr. E. B.

Matthews and includes a list of the works and maps published relating to the physiography, geology and mineral resources of the state, from 1526 to 1896, inclusive, and Part v is the first report by Mr. L. A. Baur on the magnetic work in Maryland, including the history and object of magnetic surveys in general.

Volume ii, in addition to the state geologist's administrative report on the operations of the survey during 1896, and during 1897, contains in Part ii an elaborate paper by Messrs. George P. Merrill and Edward B. Matthews, on the Building and Decorative Stones of Maryland, illustrated by beautiful colored pictures of some of the more important stones as polished, and micro-photographs of their structure. Part iii is an equally elaborate report on Cartography, to which Mr. Gannett, of the United States Geological Survey which is coöperating with the state survey, contributes a valuable paper on the aims and methods of cartography; and Mr. E. B. Matthews one on the maps and mapmakers of Maryland.

The volumes are printed on excellent paper, and the illustrations are numerous and often of great beauty as works of art, and nothing seems to be spared to make the reports models of their kind.

H, S. W.

2. The Lower Cretaceous Gryphæas of the Texas Region; by R. T. HILL and T. W. VAUGHAN. Bull. No. 151, U. S. Geol. Survey; pp. 1-139, plates i-xxxv. Washington, D. C. 1898.-At last the Gryphae pitcheri Morton, and the age of the Tucumcari beds, have been set at rest. Mr. R. T. Hill has succeeded not only in solving, but in clearly demonstrating his solution of the perplexing problems regarding the Lower Cretaceous beds of Texas and neighboring regions, in showing the true order of the beds and their faunas. In this work, one of the greatest difficulties has arisen from the great variability of the Gryphæas which have served as leitfossilien, and from the confusion arising from mis-naming, and careless (or worse) state-ments regarding their occurrence and distribution. Mr. Hill, with the assistance of Mr. Vaughan, has made an exhaustive study of the whole group of Gryphæas, and determined and illustrated with numerous figures the characters of the species, their developmental history and their stratigraphic range and geographical distribution. The names of the Gryphæas (to which the name G. pitcheri has been applied) which survive the searching investigation are G. corruguta Say, G. navia Hall, G. mucronata Gabb, G. washitaensis Hill and G. Newberryi Stanton. Two new species, G. Wardi and G. Marcoui, are described. Particular attention should be called to the ontogenic study of the several species according to the Hyatt school of paleontologists.

H. S. W.

3. Bibliographic Index of North American Carboniferous Invertebrates; by STUART WELLER. Bull. No. 153, U. S. Geol. Survey, pp. 1-653, 1898.—The indexing and classifying of the innumerable facts regarding fossil species is a necessary preparation for the new paleontology, which deals with the history of organisms rather than their form and description alone. Mr. Weller has not only opened the way for his own investigation in this direction, but has rendered a great service to all advanced students who are engaged in paleontological investigation. The matter is well arranged and the necessary statistics are given with precision and will enable the student to turn at once to the original sources of information. H. S. W.

4. Contributions to the Tertiary Fauna of Florida, etc.; by WM. H. DALL. Vol. iii, Part iv.—I, Prionodesmacea: Nucula to Julia, II, Teleodesmacea: Teredo to Erville; (Trans. Wagner's Free Inst. of Sci. of Philadelphia), pp. 571-947, plates xxiii-xxxv, April, 1898.—This volume maintains the characteristics of its predecessors;—the beautiful, sharply-defined illustrations and the clear and exhaustive descriptive parts, which are carried out in many cases to a thorough revision of classification of the larger divisions and the distribution of the known species, leave little to be desired in the discussion of such a group of fossil mollusca.

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5. Contributions to Canadian Paleontology; by J. F. WHIT-EAVES; vol. i, part v, pp. 361-436, plates xlviii-l; Geol. Survey of Canada, No. 659, 1898.—This closing part of the first volume of contributions to Canadian Paleontology is chiefly concerned with the thorough revision of the nomenclature and faunas particularly noted in the previous portions of the volume, the first of which was issued in 1885.

In the first papers, the Hamilton fauna of Thedford, Widder and neighborhood in Ontario is thus revised; the additions are based upon new collections made by Mr. Schuchert, for the National Museum, in 1895 and Canadian collections examined by the author; and the revision of nomenclature is of particular importance as expressing the comparative study, of both Mr. Whiteaves and Mr. Schuchert, on large and widely distributed collections. The final list recognizes 226 species in the fauna. The second number of the part is an appendix on revision of nomenclature and statements in previous numbers of the volume. The volume being now complete, a special title page is issued with directions for binding the whole. H. S. W.

6. Geological Survey of Canadu, G. M. DAWSON, Director, Ann. Rept. (new series), vol. ix, for 1896, pp. 816, five maps, twenty plates, Ottawa, 1898,—In addition to the summary report (614) of the operation of the survey for the current year 1896, the volume contains Tyrrell's report on the Doobaunt, Kazan and Ferguson rivers, etc. (part F), Bell's report on the French river sheet (I), Low's report on the northern part of Labrador peninsula (L), Bailey's report on S. W. Nova Scotia (M), Hoffmann's report on Chemistry and Mineralogy (S) and Ingall's report on Mineral Statistics. All of them except the Tyrrell report have been previously noted (see this Journal, iii, p. 421; iv, 78, 232, 434 and 510). 7. Report on the Doobaunt, Kazan and Ferguson Rivers and the Northwest Coast of Hudson Bay, etc.; by J. B. TYRRELL. Geol. Surv. of Canada, Ann. Rept. 1896, vol. iv, part F, pp. 1-218, plates i-xi and three maps, 1897.—This report gives account of explorations carried on during the years 1893 and 1894, in a region lying north of the 59th parallel of latitude and west of Hudson Bay, covering about 200,000 square miles. It contains much valuable geological information; a study of the movement of glaciers over the region; appendices on Chippewyan and inland Eskimos vocabularies; and a third one on plants collected by J. W. Tyrrell.

8. Rivers of North America, a reading lesson for students of geography and geology; by IsrAEL C. RUSSELL; pp. 1-327, figures 1-23, plates i-xvii. New York, 1898 (G. P. Putnam's Sons) .- Prof. Russell's "Rivers of North America" is a fit companion for "Lakes of North America," "Glaciers of North America" and "Volcances of North America" by the same author. It is a delightful "reading lesson" for any one interested in geography or geology and will make brooks and rivers more attractive to the lover of nature. The characteristics of stream action are presented clearly in plain language without detailed discussion of laws or theories, and each point is illustrated from American rivers. The chapters on "Stream Development" and "The Life History of a River" trace the stream's history from youth to old age, tell of its birth, its efforts to adjust itself to its environment and the accidents which it may suffer. The river is made to appear as a thing of life. Students who have searched through manuals, geological reports and scattered essays for facts and laws of stream action will be thankful for the discussion of these subjects here given. H. E. G.

9. Earth Sculpture or the origin of land forms; by JAMES GEIKIE; pp. 1-397, pl. i-ii, figs. 1-89. New York, 1898 (G. P. Putnam's Sons).—This volume is the latest number of The Science Series published by the Putnams. The book treats first of the agents of denudation and the resulting land forms in regions of horizontal, inclined, folded and displaced strata. After this the modifying effects of igneous, glacial and æolian action on surface features are discussed. "Coast Lines" and "Classifications of Land Forms" are very useful chapters. The book is addressed to the average student who may desire some general knowledge of the development of land forms, and we know of no other English work which gives a general account of the whole subject. To American readers some of the terms and descriptions of foreign localities will seem unfamiliar and the glossary in the Appendix will be needed. This is particularly true of the divisions of the Geological Time Scale.

As an introductory treatise Prof. Geikie's book is very welcome and students of nature who have mastered this will read Sir A. Geikie's "Scenery and Geology of Scotland," Lubbock's "Scenery of Switzerland," Powell's "Canyons of the Colorado" and other physiographie classics with added interest. H. E. G. 10. Elemente der Gesteinslehre, von H. ROSENBUSCH. 8vo, pp. 546. Stuttgart, 1898.—This book is based, as the preface states, on the lectures of the author at Heidelberg. While it claims to be only an elementary treatise, it is much more than that, and will be read with interest by every petrologist as giving the latest views of its author and an excellent résumé of the present state of the science from a certain, rather subjective, standpoint.

After an introductory chapter on the general principles of petrography and the composition, structure and classification of rocks, the author describes not only the igneous rocks, to which his previous volumes have been devoted, but also the sedimentary rocks and crystalline schists.

In the portion devoted to the igneous rocks, the essexites, shonkinites and missourites have been raised to the rank of groups of the same order as the granites. The monzonites, for which Brögger has proposed a similar position, are left as a subdivision of the syenites, while among the effusive rocks a group of trachydolerites has been formed. These, according to Rosenbusch, are homologous with the essexites, but, though they resemble these in being intermediate, the examples and analyses which are given resemble more closely Brögger's monzonites. The necessity for the recognition of such groups of intermediate rocks is urgent, but this group, as here given, is the least satisfactory of all, embracing as it does many types which differ much among themselves, and it seems probable that it will undergo many changes and subdivisions in the future. It may be suggested that the name *latite* previously proposed by Ransome seems preferable to the coextensive term of trachydolerite used by Rosenbusch.

The sedimentaries are very fully and satisfactorily treated and the same is true of the metamorphic schists. For schists derived from igneous rocks the author proposes the use of the prefix *ortho*, and for those derived from sedimentaries the prefix *para*, so that we would have orthogneiss, paragneiss, etc.

In general the views held by the author are the same as those expressed in his previous works. The age distinction is practically banished, but traces of it still survive among the effusives.

The chemical characters of the various rocks are discussed in considerable detail, and a valuable feature is the insertion of tables of typical analyses, not only of the rocks themselves but of their component minerals, many of which are published here for the first time. They are in general well selected, but the almost total lack of references throughout the book, especially for the analyses, is to be deplored, even though such omissions are due to the elementary character of the work.

But such criticisms are chiefly matters of personal opinion, and the name of the author is sufficient guarantee for the high character of the volume. It should prove a valuable text-book for the German-reading student, and will be a much used addition to the library of every petrologist. H. s. w.

11. The Educational Series of Rock Specimens collected and distributed by the U. S. Geological Survey; by J. S. DILLER. Bulletin No. 150, U. S. Geol. Surv., Washington, 1898, pp. 400, 47 pl.; price 25 cts.-A number of years ago the United States Geological Survey undertook the praiseworthy task of collecting and distributing to our leading educational institutions, as an aid in geological teaching, a series of rock collections illustrating the petrology of the United States. Under the able management of Mr. J. S. Diller, aided by many geologists both of the Survey staff and from other portions of the country, this task was sucessfully completed, and about 250 sets, comprising over 150 specimens in each, were distributed. In addition, to supplement the value of these collections, the Survey has now issued the volume above mentioned, in which the rocks are described from the standpoint of modern petrography. Under the editorship of Mr. Diller, who also contributes largely to the descriptive matter, the rocks have been described by a number of specialists, in great part those by whom they were collected, and to whom is due our knowledge of the geology of the regions in which they occur.

The method of classification is simple and rational, and the volume constitutes in fact an excellent practical text-book of petrology for Americans, and as such will be found of very great service to teachers of geology, as well as to those engaged in the more specialized petrographical branches. Its appearance in connection with the use of the collections cannot fail to give an impulse to the study of petrography, and the Survey staff in general, and Mr. Diller in particular, deserve great credit for the completion of this useful and public-spirited work. L. V. P.

12. The Mechanical Composition of Wind Deposits; by JOHAN AUGUST UDDEN, pp. 1-69. Augustana Library Publications, No. 1. Rock Island, Ill., 1898.—The author has carried on a long series of observations in order to show the part played by the air in motion in transporting sand deposits to different distances as determined by their size. Four classes are especially recognized: (1) lag gravels or coarse residue deposits in the rear of sand dunes; (2) drifting sand, constituting the sand dunes of dry and sandy regions; (3) fine sand, soon dropped by the wind in the lee of drifting dunes; (4) atmospheric dust, which only slowly settles out of the air far away from the place where it was raised.

Many observations in regard to each of these have been made at different points, chiefly in Illinois, Indiana, Nebraska, Kansas and the Dakotas. The results, given in the form of numerous tables, show the percentage of particles of characteristic size present under the given conditions. For example, lag gravels, though varying widely in different localities, include chiefly particles from 4<sup>mm</sup> to 4<sup>mm</sup> in diameter; drift sands those from 1<sup>mm</sup> to  $\frac{1}{5}$ <sup>mm</sup>; dune sand is more uniform, from 60 to 70 or 80 per cent of the particles ranging between 4 and  $\frac{1}{5}$ <sup>mm</sup>; lee sand runs down to  $\frac{1}{5}$ <sup>mm</sup> or smaller, and atmospheric dust varies from 4 to  $\frac{1}{25}$ <sup>mm</sup> and smaller. The approximate maximum distances over which quartz fragments may be lifted by moderately strong winds in single leaps are estimated as follows:

Gravel (8-1 <sup>mm</sup> diam.)	A few feet.
Coarse and medium sand $(1-\frac{1}{4})$	Several rods.
Fine sand $\left(\frac{1}{4} - \frac{1}{8}\right)$	Less than a mile.
Very fine sand $\left(\frac{1}{8} - \frac{1}{16}\right)$	A few miles.
Coarse dust $\left(\frac{1}{16} - \frac{1}{32} \right)$	200 miles.
Medium dust $\left(\frac{1}{32} - \frac{1}{64} \text{ mm}\right)$	1000 miles.
Fine dust $\left( \begin{smallmatrix} 1 & mm \\ 64 \end{smallmatrix} \right)$ and less)	Around the globe.

A striking result brought out is the comparative definiteness with which the different grades are separated from each other by the sorting action of the wind. In closing, the author discusses briefly the relation of the facts brought out by his investigations to the origin of the loess deposits, which in their mechanical composition certainly resemble atmospheric sediments. He does not regard it possible, however, to reach a final conclusion from the data at hand.

13. Brief notices of some recently described Minerals.—SENAITE is a new mineral, related to ilmenite, described by Hussak and Prior. It is found in rounded fragments and rough crystals in the diamond-bearing sands of Diamantina, Minas Geraes, Brazil. Crystallization like ilmenite, rhombohedral-tetartohedral (trirhombohedral). Hardness about 6, specific gravity of crystals, 5:30, massive 4:78 to 4:22; luster sub-metallic and color black, in thin splinters, greenish. Analysis gave :

TiO<sub>2</sub> Pb0 FeO Fe<sub>2</sub>O<sub>3</sub> MnO MgO SnO. 20.22 G\_\_\_4.78 57.21 10.51 4.14 7.00 0.49 0.11=99.68 The formula (Fe, Pb) O.2(Ti Mn) O, is suggested, but doubtful.-

Min. Mag., xii, 30, 1898. Mossitte is a name given by Brögger to a nisbo-tantalate of iron occurring with yttro tantalite at Moss, Norway. It is found in black tetragonal crystals with  $\dot{c} = 0.644$ . The crystals are mostly twins with (101) as twinning plane; they are often distorted by elongation parallel to (111) as is sometimes observed with rutile. An analysis gave (N6,Ta)<sub>2</sub>O<sub>6</sub> 82.92, FeO 16.62, SnO<sub>2</sub> 0.18 = 99.72, which corresponds to the formula Fe (N6, Ta)<sub>2</sub>O<sub>6</sub>; further it was found that N6 : Ta = 1: 1. The author shows that mossite is near tapiolite, which, however, is richer in Ta<sub>2</sub>O<sub>6</sub> and has  $\dot{c} = 0.652$ . He has also made the interesting observation that the crystals of "tantalite" which have long been figured in the text-books, are in fact identical with tapiolite, being twin crystals similar to those mentioned above.— Vid. Skrift. Math.-nat. Klasse, 1887.

VALLÉITE is a mineral closely related to anthophyllite occurring with the violet tremolite of Edwards, N. Y.; it is described by G. Cesàro. Crystallization orthorhombic; occurs in colorless prismatic crystals with the usual amphibole angles of 125° 30' and 54° 30'. The cleavage is prismatic and pinacoidal. The hardness is 4.5, specific gravity 2.88. Analysis gave :

The formula is  $RSiO_{s}$ , or that of anthophyllite, from which it is stated to differ somewhat in optical characters ( $\gamma - a = 0.0036$ ).— *Zeitschr. Kryst.*, xxx, 84.

CEDARITE is a fossil resin, resembling amber, from the alluvium of the Saskatchewan river, Canada. Analysis gave: C 78·15, H 9·89, S 0·31, O 11·20, ash 0·45 = 100. Described by R. Klebs, *Jahrb. Min.*, ii, 212 ref., 1898.

BATAVITE, described by Weinschenk, is a decomposition product occurring with the graphite deposits near Passau, Bavaria. It occurs in white pearly scales with a specific gravity of 2'183. Analysis gave: SiO<sub>2</sub> 42'33, Al<sub>2</sub>O<sub>8</sub> 16'35, MgO 28'17, H<sub>2</sub>O 13'19 = 100'04. For this the composition suggested is H<sub>8</sub> Mg<sub>4</sub> Al<sub>2</sub> Si<sub>4</sub>O<sub>19</sub>.— Zeitschr. Kryst., xxviii, 160.

GRÜNLINGTTE, described by Muthmann and Schröder, is a sulpho-telluride of bismuth, related to tetradymite, from Cumberland, England. It was earlier investigated by Rammelsberg, but the authors have obtained on analysis a composition agreeing with the formula Bi<sub>4</sub>S<sub>4</sub>Te or Bi(S, Te). It appears in cleavable masses with metallic luster and gray color; the specific gravity is 7-321. Named after Dr. F. Grünling of Munich.—*Ibid.*, xxix, 144.

PLANOFERRITE, described by L. Darapsky, is a hydrated ferric sulphate from the Lautaro copper mine in Atacama. It occurs in tabular crystals which are colorless or lemon-yellow. An analysis gave: SO<sub>3</sub> 15:57, Fe<sub>2</sub>O<sub>3</sub> 31:20, H<sub>2</sub>O 51:82, insol. 1:41 = 100. This corresponds to Fe<sub>2</sub>O<sub>3</sub>. SO<sub>5</sub>. 15 H<sub>2</sub>O. *—Ibid.*, xxix, 213.

#### III. BOTANY AND ZOOLOGY.

1. The Poisonous effect exerted on living plants by Phenols. (Botan. Centralblatt, Nov. 15, 1898.)-Professor R. H. TRUE has extended his fruitful investigations respecting the action of toxic substances far beyond the boundaries which he originally marked out. With efficient collaborators, he studied two years ago the effects of salts, acids, and bases, on one of the Leguminosæ, and had the satisfaction of having the results substantially confirmed by other experimenters, and the suggestions carried into a wider field. With Mr. Hunkel, he returns to the task, and obtains results which appear to confirm the belief that the whole subject of Toxicology is to receive abundant light from the study of plants. It is well known that the meagre information regarding the action of active remedial agents on plants, embodied in the Dispensatories, is unsatisfactory, but it certainly indicates a desire on the part of the commentators to get what little light glimmers through the obscure experimentation. Now, of late years, the whole subject has been placed on a different basis, and the work done upon this basis is creditable alike in its suggestion and its execution. It is not yet time to summarize the details or

attempt their complete co-ordination, but it is not too soon to predict that materials will before long be sufficient for a rational discussion of many obscure points in Toxicology and, we dare to hope, in Therapeutics. To the energy and carefulness with which Dr. True has prosecuted his work thus far, we owe most important contributions, and we trust he will be encouraged to carry his researches still further afield. The new paths which he has been instrumental in opening up are likely to attract many explorers. It is to be sincerely wished that all who enter the new field will bring to the work the same acuteness, patience, and thoroughness which seem to characterize the work thus far. To those of our readers who may like to know the thought which inspires the work, we may use words of Dr. True, which are abundantly justified. "The application of the theory of dissociation of electrolytes to explain the toxic action of acids, bases, and salts, on living organisms has yielded results of greatest import to both chemistry and biology." Now beyond these substances others are to be investigated by the same methods: let us hope with equally satisfactory results. G. L. G.

2. On the peculiar mode of formation of pollen-grains in Magnolias.—In the number of Comptes Rendus for Oct. 24, 1898, GUIGNARD gives an extremely interesting account of one of the puzzling exceptions to general rules, which are full of suggestions as to classification of organisms.

The author calls attention to the general characters of pollen formation which serve to separate more or less completely monocotyledons from dicotyledons. In the former, the first division of the nucleus of the mother-cell is followed by partition of the latter, and then the two daughter-cells divide in their turn, in the same way. In dicotyledons, on the other hand, the first nuclear division is not followed by partition of the mother-cell; that does not take place until after the second nuclear division, between the four nuclei which it has furnished.

Now to this general rule, Guignard had already pointed out a remarkable exception, namely, that among the monocotyledons are to be found plants which behave in this respect just as do the dicotyledons. These exceptions are the Orchidaccee. They nearly all undergo simultaneous quadripartition of the pollinic mother cell. The author now announces that in the Magnolias is to be seen a type of division unlike either the first or the second. The type is almost intermediate between the two hitherto recognized, but by the formation of an incomplete partition (possibly sometimes complete) immediately after the first nuclear bipartition, is more like that of the monocotyledons than of the dicotyledons. G. L. G.

3. Elements de Botanique. P. VAN TIEGHEM. 2 volumes, 16mo. Paris, 1898.—In this revised edition of a helpful work, Professor Van Tieghem gives his own views regarding certain disputed points relative to structure, and states his reasons for suggesting a new classification of the higher plants. The principal features of this new system have already been presented in this Journal, and therefore need not be again spoken of in detail. But it seems proper to mention the fact that Professor Van Tieghem's system, although distinctly revolutionary, appears to offer advantages in practical ways, especially in bringing out clearly the disguised resemblances. The author has done good service in emphasizing a good many things which have been more or less overlooked in previous systems. It is not improbable that some of these things have been insisted on rather too strongly, and in this way, may throw the system somewhat out of proportion, but thus far, this does not seem to be the case. At any rate, the sense of general proportion is good, and, as a natural result, the perspective is not misleading. Teachers will find a good many fruitful suggestions in every part of the two volumes, but most of all in the portion devoted to classification. G. L. G.

4. Sketch of the Evolution of our Native Fruits; by L. H. BAILEY; pp. xiii+472, 125 figures in text. New York, 1898 (The Macmillan Co.).-During the past ten years Professor Bailey has made a study of our indigenous fruits and of the cultivated varieties to which they have given rise. Some of the results of his investigations have already appeared in periodicals, and the present volume brings these scattered observations together and presents the whole subject in a more complete and connected form. The greater part of the book deals with the more important of our fruits, those which are most widely cultivated and which are consequently represented by the greatest number of cultivated varieties. These include the grape, the mulberry, our native plums, cherries and apples, the raspberry, the blackberry and the The chapter on the grape, though particularly dewberry. exhaustive, may indicate the scope of the work: in addition to a history and description of our various native grapes and of their cultivated varieties, it gives an account of the early attempts and failures to introduce the European grape into eastern America and concludes with a full bibliography of American grape literature. At the close of the book some attention is paid to our less important fruits, the gooseberries, currants, etc., which, although less widely cultivated, offer considerable promise to the cultivator.

A. W. E.

5. Bush-Fruits: a Horticultural Monograph of Raspberries, Blackberries, Devberries, Currants, Gooseberries, and other Shrublike Fruits; by FRED. W. CARD; pp. xii+337, 113 figures. New York, 1898 (The Macmillan Co.).—The present book is the first of a proposed series of monographs dealing with the various types of American fruits. As its title indicates, it is distinctly horticultural and devotes its chief attention to a description of the varieties of the "bush-fruits" enumerated and of the methods employed in their cultivation. A. W. E.

6. The Metamorphosis of Asterias pallida [A. vulgaris] with special reference to the fate of the Body Cavities; by S. Goto. Jour. College Science Imp. Univ. Tokyo, Japan, vol. x, pt. iii, pp. 239-278, pl. xix-xxiv, 1898.—This important paper relates to the common northern starfish of New England. It is the result of work done at the Newport laboratory of Mr. A. Agassiz and at the Museum of Comp. Zoology of Harvard University. v.

7. Zoological Results based on material from New Britain, New Guinea, Loyalty Islands, and elsewhere, collected during 1895-1897; by ARTHUR WILLEY. Part I. Cambridge, Eng., Univ. Press.—The first article consists of a very detailed account of the development and anatomy of Peripatus Novæ-Britanniæ, sp. nov., illustrated by four plates. The second is devoted to a new species of Caprellidæ (Metaprotella Sandalensis). The third is on a sea-snake from the South Pacific, Aipysurus annulatus (Kraftt), with figure. The fourth is a Report on the Centipedes and Millipedes, pl. vi. The fifth is on the Phasmidæ with notes on the eggs, pl. vii-ix. The sixth paper relates to the Pedapalp and Scorpions, pl. x, xi. v.

8. An Account of the Crustacea of Norway, with figures of all the species; by G. O. SARS Vol. II, parts xi, xii. Oniscidæ, Bopyridæ, Dajidæ; 4to. Bergen. Published by the Bergen Museum, 1898.—This is a continuation of the admirable work of Professor Sars on the Norwegian Crustacea. This part contains eight autographic plates drawn by Dr. Sars himself, with his customary care and accuracy. This work is of special interest to American naturalists, because a considerable percentage of the species will be found also on our coast. v.

<sup>9</sup>9. The Mollusca of the Chicago Area: The Pelecypoda; by FRANK COLLINS BAKER, pp. 1-130, with 27 plates. The Chicago Academy of Sciences, Bulletin No. iii, Part i of the Natural History Survey, Sept. 1, 1898.—This exhaustive and liberally illustrated memoir by Mr. Baker has recently appeared. A second part, devoted to the Gastropoda, is promised.

10. Catalogus Mammalium tan viventium quam fossilium a Doctore E.-L. TROUESSART, Parisiis. Nova Editio (Prima completa). Fasciculus IV, pp. 665-998; V, pp. 999-1264. Berlin, 1898 (R. Friedländer & Son).—Parts i-iii of the exhaustive Bibliography of papers relating to living and fossil mammals, by Dr. Trouessart, have already been announced in our pages. Parts iv and v have now appeared, embracing some six hundred pages and bringing this important work to a close. Part iv includes the Tillodontia and Ungulata: Part v the Sirenia, Cetacea, Edentata, Marsupialia, Allotheria, and Monotremata. The genera included in these two parts extend from Nos. 761 to 1588, and the species from Nos. 4086 to 7224; and besides there are many varieties not separately numbered. The whole bibliography is printed with admirable clearness.

11. The Fishes of North and Middle America; by DAVID STARR JORDAN and BARTON WARREN EVERMANN; pp. i-XXX, 1241-2183. Washington, 1898 (Bulletin 47 of the U. S. National Museum, Smithsonian Institution).—Part II of the complete descriptive catalogue of the fishes found in the waters of North America north of the Isthmus of Panama, by Jordan and Evermann, has recently been issued. Part I was published in October, 1896. The third and final part with index, glossary, etc., is promised soon; it will be followed by a fourth volume which will be an atlas of plates.

## IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Institute of France.—At the session of the Académie des Sciences held at Paris, December 5, 1898, Professor O. C. Marsh of Yale University, to whom the Cuvier prize was awarded a year since, was elected Correspondent of the Academy.

2. Annual Report of the Board of Regents of the Šmithsonian Institution showing the operations, expenditures and condition of the Institution to July, 1896; pp. i-li, 1-727; plates i to lxi.— This valuable report submitted to Congress by the Secretary, S. P. Langley, has recently appeared. The opening portion (pp. 1-77) are given to matters of administrative detail in regard to the work of the Institution in its different departments. The General Appendix (pp. 89-727) contains as usual a series of scientific papers on a wide range of topics, the republication of which in this place is a boon to many interested in science.

3. Der Ursprung der Afrikanischen Kultur von L. FROBENIUS, pp. i-xxxi, 1-368, with 5 folded charts, 9 plates and 225 illustrations in the text. Berlin, 1898 (Gebrüder Borntraeger).—This is the opening volume of what promises to be an extensive and important work, devoted to the origin of culture in general. The subject of the volume is the origin of culture in Africa, and this is treated with much fullness and abundance of illustration. Some of the topics discussed in detail are the weapons, shields, knives, etc.; also the various kinds of musical instruments, the different forms of huts and household utensils. The latter portion of the work deals with the physiological side of the subject in its varied aspects.

4. Organic Evolution Considered; by ALFRED FAIRHURST, pp. 1-386. Christian Publishing Co., St. Louis, 1897.—In regard to his work the author states: "I look upon the theory of evolution as being of no importance except as it involves the wellbeing of man. . . My object in what I have written is to promote the belief in theism and in the existence of a spiritual nature in man which theism alone can explain."

Catalogues recently issued.

Catalogue of Books and Papers on Chemistry and Physics, No. iv. Dulau and Co., 37 Soho Square, London, W., 1898.

Dr. F. Krantz, Rheinisches Mineralien-Contor in Bonn.—Katalog Nr. la (Siebente Auflage), Mineralien and Mineralpräparate, Mineralogische Apparate und Utensilien, pp. :-xii, 1-113, 1898. Catalogue and Price List of Minerals for Scientific and Educational Purposes.

Catalogue and Price List of Minerals for Scientific and Educational Purposes. Loose crystals a specialty. Roy Hopping, 5 and 7 Dey Street, New York City. 1889.

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WITH PLATE I.

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## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

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#### ART. X.—A Contribution to the Study of Contact Metamorphism; by J. MORGAN CLEMENTS.

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THE various Huronian sediments which form a great portion of the iron-bearing districts of the Upper Peninsula of Michigan have in all of these districts been found to be penetrated by dikes of igneous rocks, which are predominately basic in character. The influence which these dikes exert in the formation of ore bodies where they cut the iron-bearing formations has been carefully worked out and described by Van Hise in numerous papers. The effects of contact metamorphism produced by the dikes upon the intruded sediments are of much less economic importance, and, to a very considerable extent, have been overlooked. In this paper I shall describe the products which have resulted from the intrusion of basic dikes in the Mansfield slate formation, a Lower Huronian iron-bearing formation of the Crystal Falls district of the Upper Peninsula of Michigan.\*

The Mansfield formation, in its typical development, occupies a narrow valley, about three miles in length, through which flows the Michigamme River. In this valley there is situated the village of Mansfield and the mine of the same name. The formation consists of graywackes, slates (these predominate, hence the name), and phyllites, of demonstrably sedimentary origin. Associated with these, either as beds or

\* For details concerning the position which the Mansfield formation holds with reference to the other Huronian rocks, the reader is referred to an article entitled The Crystal Falls Iron-bearing District of Michigan, soon to be published in the 19th Ann. Rept. U. S. Geol. Survey, and in a Monograph of the Survey.

AM. JOUR. SCI.-FOURTH SERIES, VOL. VII, NO. 38.-FEBRUARY, 1899.

as lenses agreeing in strike with the sedimentaries, we find slaty siderite, ferruginous chert and iron ore. The origin of the siderite and chert cannot be stated with certainty. The ore was derived from them by processes of metasomatism and concentration. All of these rocks, wherever exposed, are found to strike north and south, with at times slight variations from this direction, probably due to minor crumpling of the formation. The dip is high to the west at about 80°.

Overlying the Mansfield slates is the volcanic Hemlock formation.

Immediately east of the slates, that is, stratigraphically under them, there occur continuous masses of coarse dolerite (diabase), which cut off the slates in their strike, both to the north and to the south. No well-characterized dikes of dolerite cutting the Mansfield formation have thus far been found, either by surface studies or by underground exploration. In no instance, moreover, has a direct contact between the dolerites and the slate formation been observed, owing to the contacts being covered by disintegration products, although in many instances these rocks are separated from each other by spaces only a few feet in width. That the relations between the two, however, are those of igneous intrusion, is shown by the fact that the dolerites cut across the strike of the slates. Furthermore, if we make a traverse from the dolerites westward into the slates we notice the following. On the westward flank of the dolerite ridge we find associated with the dolerites masses of hard, peculiar, hornstone like rocks, which have a well-banded character and in places are of large size and very numerous. Leaving this zone we reach the valley proper, in which lie the normal sedimentaries of the Mansfield formation. It thus appears that we have an intermediate zone between the dolerites and the slates. The banded rocks forming, with the associated dolerites, this intermediate zone, are believed to be sedimentary rocks which have been metamorphosed by the dolerites.

The exact original characters of these sedimentary rocks cannot be stated with positiveness. They are believed to have been slates having essentially the same general physical characters and mineral and chemical composition as the slates which now lie next to the contact zone and extend away from it for several hundred feet across the strike, without showing any noticeable changes in character. Although original chemical variations exist in these slates, as is shown by the banding, and did exist in the slates from which the metamorphosed products to be described were derived, as is shown by the banding in . them,—nevertheless, such initial variations in these rocks is of a quantitative rather than qualitative character, and it is not believed that they can vitiate the conclusion concerning the effect of the metamorphic action upon the slates.

In the further discussion, therefore, it is assumed that the noteworthy differences between the rocks to be described are due to metamorphic action, and are not due to the original chemical differences. This assumption seems to be warranted by the fact that the changes are in perfect accord with those described from similar dolerite-slate contact zones in other areas.

The products of the contact metamorphism are those banded and spotted rocks which have been called spilosites, desmosites, and adinoles, and they will be the special subject of this article.

The dolerites (diabases) are coarse-grained, and do not exhibit anything of especial interest, consequently no description will be given of them. No evidence of any endomorphic action whatever has been observed in them.

In a study of contact action it is, of course, of the greatest importance to be able to determine accurately the order of succession from the unmetamorphosed to the most metamorphosed forms of the rocks. In the present case it is impossible to compare sections from, or analyses of, any given stratum of the rock at successive stages of approach to the line of contact, for the reason that, where the exposures were found, the dolerite had been intruded parallel to the strike of the slates. Moreover, the exposures are very poor, indeed. This order of succession has, however, been made out so satisfactorily for other localities by Lossen and others, and the characters of each rock in the succession have been so well described, that I have no hesitation, after microscopical study of thin sections of the specimens, in presenting the series in the following order. Beginning with the clay-slate, the least metamorphosed rock in the district, and the ones farthest removed from the intrusives, we pass to the phyllites, then to the spilosites and desmosites, and finally to those which are known as adinoles, the latter being those which occur next to the intrusive.

#### The Clay-slates.

These are dull and lusterless banded rocks, ranging in color from black to olive-green and red. They are usually impregnated with more or less iron pyrites in large macroscopical erystals. By high power, one can very readily distinguish in the slates round or oval areas of limpid quartz, surrounded by a dark grayish mass, which consists of minute flakes of white mica, erystals of rutile, and some of hematite, here and there a long, transversely-fractured, greenish needle, taken for actinolite, and, lastly, a dark grayish to black granular aggregate, which is the chief coloring matter of the slate, and which makes up a very considerable part of the rock. This aggre

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gate is presumed to be of clastic origin, and to be chiefly feldspathic dust, darkened by carbonaceous and ferruginous specks. Careful search was made for flakes of chlorite and biotite, but no traces of either mineral could be found. Likewise, feldspar is absent in grains or crystals of a size which could be recognized. The banding of the slates is occasioned by the varying quantities of these minerals, although each band contains some individuals of all the kinds enumerated. All the crystals lie with their long axes parallel, causing the cleavage of the slate. It is clear that the slate is already in what we may perhaps call a semicrystalline state, the crystals of white mica, actinolite and rutile evidently being new developments in the sediments.

Origin and composition of the clay-slates.—The origin of the clay-slates of the Mansfield formation is probably to be looked for in the disintegration and decay of the Archæan granite and the subsequent compression of the resulting clay; for between the Archæan granites and the Mansfield slates no other rock masses are known to have existed in this region from which the clay could have been derived.

An examination of series of analyses of granites shows that while the relative percentages of soda and potash vary considerably, on the whole the potash is the higher of the two.

As a consequence of the easier solubility of the soda, this relation between the alkalies, soda and potash, is maintained, and is often very striking in clay-slates. An average of thirtyone analyses of clay-slates taken from various sources shows two and one-half times as much potash as soda. In the case of the Mansfield slate, it will be seen that the difference is much greater, there being present ten times as much potash as soda.

ANALYSIS OF MANSFIELD SLATE.								
(	Вy	Mr.	Geo.	Steiger,	U.	S.	G.	S.)
SiO,								60.28
TiO.								. •69
ALC								22.61
Fe <sub>.</sub> O								2.53
FeO	• • - ·							•45
MnO								trace
CaO								•13
BaO								•04
MgO								1.35
K.O								5.73
Na.O								•54
H.Ő :	at	100	_					·60
H <sup>2</sup> O	at	100	+					3.62
PO								.03
$CO^{2}$								none
C								.97
_	-							

Total 99.57 The relative proportion of the alkaline earths, lime and magnesia, is also striking, the latter being present in the greater quantity. As a general rule, in igneous rocks (and to igneous rocks all clay-slates owe their ultimate origin) the reverse condition exists, i. e., the magnesia is subordinate in quantity to the lime, except in the ultra basic non-feldspathic kinds. The carbon present in this slate is considered as offering trustworthy evidence of the presence of organic life at the time of the deposit of the slates, though no more satisfactory evidence of the existence of life thus early has ever been found. It will be noticed finally that considerable water is present, but in consideration of the character of the rock this is to be expected, and if anything the value is low. These clay-slates are the rocks which are nearest the original sediments.

#### Phyllites.

The phyllites have a silky luster and bluish black color. They are composed essentially of white mica, which occurs in large quantity surrounding grains of quartz and feldspar (?). Rutile occurs in single crystals and in clumps of small crystals scattered through the mica. Associated with it, there occur here and there flakes of hematite, and small aggregates of black, undeterminable specks. Apparently, no interstitial material, such as occurs in the clay slates, is here present.

These rocks seem to differ from the clay slates only in that they are more completely crystalline, the interstitial material of the slates having disappeared. Owing to the apparently unimportant differences which exist between the clay-slates and the phyllites, no analyses have been obtained of the latter.

#### Spilosites, Desmosites, and Adinoles.

With these rocks we begin the consideration of the true contact products of the dolerite. These contact rocks possess certain characters in common. They are dense, flinty, "hornstone-like" rocks, which in some cases still show the fine banding of the original slates. Others are very characteristically spotted. They have a splintery, and at times almost conchoidal fracture, and vary in color on fresh fracture from light to very dark gray and greenish. The weathered surface, in almost all cases, is covered by a thin, white to light yellowish erust. The mineralogical components are quartz, feldspar (albite), biotite, chlorite, white mica, actinolite, rutile, epidote, and iron oxide. Various combinations of these minerals occur, and likewise the textures vary. As a result of these variations there are produced the different kinds of contact products known as spilosites, desmosites, and adinoles. The characters of the minerals showing nothing unusual, I shall briefly describe the textures and mineral combinations which characterize these various rocks.

Spilosites—The ordinary spilosites are distinctly mottled in the hand specimen, and show clearly to the naked eye in thin section the oval spots which characterize them. These oval areas are very commonly four millimeters long, and in rare cases even longer. They are frequently connected, forming chains. The spots are very appreciably darker than the mass in which they lie, and are composed of aggregates of chlorite, quartz, feldspar, and rutile, with a small amount of white mica. The chlorite is the chief constituent of the spots and gives them their dark color. The surrounding mass consists essentially of white mica, quartz and feldspar, small epidote and rutile crystals, flakes of hematite, and with a very slight amount of chlorite. The different proportions of chlorite and muscovite cause the difference between the spots and the groundmass. In some of the spilosites we find a few flakes of biotite and needles of actinolite. However, these are always very subordinate in quantity to the chlorite.

Other spilosites have been noted in this area in which the spots are white and lie in a fine-grained dark mass composing the greater part of the slides. So far as I can learn, only one similar instance of the occurrence of such a variety of spilosite has been described. This is by Van Werveke, to whose description reference is made by Zirkel\* and Rosenbusch.<sup>†</sup>

The white spots are composed essentially of feldspar, with only a minor amount of chlorite and epidote. The feldspar grains are much larger than those which take part in the constitution of the mass surrounding the spots. This surrounding mass is made up of quartz, feldspar, chlorite, epidote, some sphene, with sheaves of actinolite scattered through it. In one section flakes of biotite were observed mixed with the chlorite, though in very subordinate quantity.

<sup>\*</sup> Zirkel. Lehrbuch der Petrographie, 2d edition, vol. ii, 1894, p. 719.

<sup>+</sup> Rosenbusch, Mikroskopische Physiographie, 3d edition, vol. ii, 1896, p. 1127.
	1.	2.
iO	52.51	57.77
CiO <sup>2</sup> ,	1.70	.92
۵۱٫Ő,	19.00	19.35
Cr.O.,	none	none
Te, O,	3.31	1.29
YeO	7.19	3.37
InO	trace	trace
CaO	1.55	1.71
BaO	trace	none
rO	trace	trace
IgO	3.29	4.35
ζΟ	.70	.22
(a.O	6.72	8.22
j.Ö	trace	none
I O at 110°	•34	·18
I <sup>2</sup> O above 110°	3.26	2.34
°.0,	•15	.04
Ö_°	none	none
and SO.	none	none
*		
Я	none	none
·	trace	none
Total	99.72	99.76

STADEHMOHSMANHHHOSOOE

ANALYSIS OF SPILOSITES.

No. 1, Spilosite, Spec. 32861 Lake Superior Division U. S. Geol. Survey, from Mansfield, Michigan, Dr. H. N. Stokes, analyst.

No. 2, Spilosite, Spec. 32827 Lake Superior Division U. S. Geol. Survey, from Mansfield, Michigan, Dr. H. N. Stokes, analyst.

Desmosites .- Under the desmosites are included contact products composed of the same mineral constituents as the spilosites, but which instead of being spotted show a distinctly banded structure. That these are very closely related to the spilosites, and that in fact they grade into each other is shown by the study of one rock. A section from this, examined under the microscope, shows irregularly rounded areas which consist of ragged bunches of chlorite and aggregates of rutile and epidote, with some flakes of biotite lying in a quartz-feldspar mass. As these spots increase in number they approach each other and unite, forming streamers which in their turn unite and form bands. No analysis has been obtained of the desmosites, as it was so evident that they contain nothing different from the spilosites.

Adinoles.-Thus far chlorite has been the chief dark constituent of the contact products mentioned, whereas actinolite is

\* C was not determined.

either totally absent or else is present merely as an accessory. In the adinoles actinolite is the characteristic constituent. The minor constituents, as a rule, are more uniformly distributed than in the spilosites. However some spots are present and are composed essentially of actinolite. The actinolite is present in sheaf-like growths, lying commonly in an exceedingly fine-grained mass of quartz and albite, with some flakes of chlorite and grains of epidote. The adinole is rendered rather dark by minute black specks which are disseminated through it. In places these are collected in irregular or lenticular heaps. They seem to be carbonaceous matter.

ANALYSIS OF ADINOLE FROM MANSFIELD, MICHIGAN.

	(By	Mr.	Geo.	Steiger	, U. S.	G. S.	)
SiO,						'	74.16
TiO <sub>a</sub>							•37
Al <sub>o</sub> Ő							11.85
FeO							.82
FeO	° 						1.66
MnO							•06
CaO							2.10
BaO						:	none
MgO							2.10
K <sub>0</sub>							.15
Na C	)						6.57
H.Ŏ	at 1	00°					.05
H <sub>0</sub>	at 1	$00^{\circ}$	+ .				.52
P.0.							.08
$CO^{2}$							•09
C <sup>2</sup>							.18
						-	
	Т	otal					100.76

Other varieties of the contact rocks.—There is still another kind of contact rock in which actinolite is the chief dark constituent, and in this the actinolite is mainly collected in bands. This rock thus corresponds to the desmosites (banded chlorite rocks) in structure, though differing from them in mineralogical composition.

The chlorite and actinolite contact rocks may be expected to grade into each other, and such a gradation is shown in one specimen, in which actinolite and chlorite are present in about equal quantity. The actinolite occurs in crystals and sheaves, forming spots; whereas the main mass of the thin section surrounding the spots is formed by chlorite as the dark silicate, associated with feldspar, quartz, and some epidote.

Comparison of analyses.—From previous determinations in other regions it is well known that the adinoles are next to the contact, while the spilosites (and desmosites) are intermediate between them and the clay-slates. The following series of analyses are arranged in the order of approach to the dolerite, as determined by the character of the rocks:

	1.	2.	3.	4.
SiO,	60.28	52.51	57.77	74.16
TiQ.	.69	1.70	$\cdot 92$	•37
Al, Õ,	22.61	19.00	19.35	11.85
Cr <sub>a</sub> O		none	none	
Fe <sub>0</sub>	2.53	3.31	1.29	•82
FeO	•45	7.19	3.37	1.66
MnO	trace	trace	trace	•06
CaO	•13	1.55	1.71	2.10
BaO	•04	trace	none	none
SrO		trace	trace	
MgO	1.35	3.29	4.35	2.10
K.O.	5.73	•70	.22	·15
Na <sub>o</sub> O	•54	6.72	8.22	6.57
Li Ö		trace	none	
H.O at 100°	·60	* •34	* .18	$\cdot 05$
$H_{0}^{2}O$ at 100° +	3.62	† 3·26	+2.34	•52
P.O.	•03	15	·04	.08
CÔ	none	none	none	.09
S and SO		none	none	
C	•97			.18
Cl		none	none	
F		trace	none	
Total	99.57	99.72	99.76	100.76

No. 1, Clay-slate, Spec. No. 32497 L.S. D., U.S. G. S. Analyst Mr. Geo. Steiger.

No. 2, Spilosite, Spec. No. 32861 L. S. D., U. S. G. S. Analyst Dr. H. N. Stokes.

No. 3, Spilosite, Spec. No. 32827 L. S. D., U. S. G. S. Analyst Dr. H. N. Stokes.

No. 4, Adinole, Spec. No. 32465 L. S. D., U. S. G. S. Analyst Mr. Geo. Steiger.

In these analyses the usual increase of silica as the dolerite is approached is at once noticeable, and hand in hand with it goes the diminution in percentage of alumina and iron oxides. The content of water and carbonaceous‡ matter also suffers diminution, as was to be expected.

The most noteworthy difference between the clay-slate and the contact rocks is shown in the relations of potash and soda. This is well brought out in an examination of analyses Nos. 1

> \*  $H_2O$  at 110°.  $\ddagger H_2O$  above 110°.  $\ddagger H_2O$  above 110°.  $\ddagger The C in Nos. 2 and 3 was not determined.$

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and 2. It will be seen that there is only about  $\frac{1}{8}$ th as much potash in the contact rocks as in the normal clay slate; while, on the contrary, about 12 times as much soda as there was in the slate has been added to the contact rock. This causes a reversal of the relations of the soda and potash, so that, whereas in the clay-slate there is present 10 times as much potash as soda, we find in the contact rock taken as an example very nearly 10 times as much soda as potash.

#### Comparison of Mineralogical Composition.

It will be sufficient for our present purpose to consider the clay-slate, on the one hand, and the spilosite and adinole on the other. To recapitulate briefly, in the clay-slate we have quartz (clastic), white mica, actinolite, rutile, and an indeterminate interstitial material of finely granular character, discolored by carbonaceous and ferruginous matter. This interstitial material we may consider as that remnant of the original feldspar, quartz, biotite, and iron ore dust in the original clay which was not used in the production of the white mica, actinolite, and rutile now found in the clay-slate. Original chemical differences in the slate are shown by the arrangement of the various materials in bands, certain bands containing a greater quantity of white mica; hence, the conclusion that these were probably richer in alkali than the adjoining bands, which are poor in white mica.

In the spilosite and adinole we find present quartz-but not clastic-white mica, actinolite, and rutile, as in the clay-slate. But in addition there is albite, chlorite, epidote, and biotite. There is nothing in these rocks which shows clastic origin. The original sediment has been completely recrystallized and there remains only the banding to point to the sedimentary origin of the rock. The clastic quartz has been destroyed by solution or aqueous fusion, and has been recrystallized, and now forms a mosaic with the albite. Albite, for whose production some of the silica of the clastic quartz may have been used, is present in the rock in considerable quantity, in contradistinction to its total absence from the slate. The initial quantitative chemical differences existing in the clastic rock are also shown in the recrystallized rock by differences in the mineralogical composition, a large quantity of chlorite, for instance, forming a band adjacent to a band poor in chlorite, thus indicating a richness of the first band in magnesium. The greatest difference existing between the practically unmetamorphosed slate and the contact product is the evidence in this last of complete recrystallization, and the presence of albite in large quantity.

#### Cause of Chemical and Mineralogical Changes in the Rocks described.

The changes which have taken place in sedimentary rocks as the result of contact with igneous rocks have given rise to a great deal of discussion. The one school, notably represented by the French geologists, contends that there is an actual transfer of material from the igneous rock to the rock intruded with more or less complete resorption of the latter; whereas the other school has maintained that the indisputable metamorphism observed in such cases is due chiefly to the action of the so-called mineralizers. Studies upon a series of contact rocks similar to those here presented have given foundation for the view upheld by Roth,\* Zirkel,† and others, that in the case of contact metamorphism produced by basic rocks an actual transference takes place. This view has been recently very strongly advocated by W. Maynard Hutchings, # who has described some interesting products, which result from the contact of the Whin Sill, which still further support it.

The very considerable changes which are shown by the above analyses to have taken place in the metamorphism of the slates, especially the change in the amount of silica and soda resulting in the production of albite in large quantity, seem to add weight to the supposition that in such contacts an actual transfer of material, possibly in the form, as has been suggested by others, of a soda silicate, does take place from the basic igneous rock to the intruded slate.

MADISON, WIS.

\* Chemische Geologie, by J. Roth: Berlin, 1890, vol. iii, p. 145. † Lehrbuch der Petrographie, by F. Zirkel: Leipzig, 2d edit, vol. ii, 1894, p. 722. † Notes on the composition of clay-slates, etc., and on some points in their contact metamorphism, by W. M. Hutchings: Geol. Magazine, vol. i, dec. 4, 1894, p. 75.

An interesting contact rock, with notes on contact metamorphism, by W. M. Hutchings: Geol. Mag, vol. ii, dec. 4, 1895, p. 122-131, 163-169.

# ART. XI. — The Origin of Mammals;\* by HENRY F. OSBORN.

SINCE the source of the Mammalian phylum was later than that of the Reptilian phylum in the Permian and possibly Carboniferous, we are sure that it extended at least very far back into the Triassic, and the Triassic was apparently a time of great continental connections and of consequent wide geographical distribution even of land types.

In presenting a phylogenetic chart which traces the ancestry of Mammals to the Upper Permian, I am quite as conscious as the most conservative zoologist present that we are not on sure ground, that this is a castle of cards liable to fall at any moment. Yet such a chart, involving as it does numberless hypotheses, is necessary to set forth certain ideas.

Clearing the way for this discussion, this chart first replaces the general view defended by Huxley in 1880, of a genetic succession between three sub-classes of mammals, which has become a matter of creed with many zoologists. In the last eighteen years not a scintilla of evidence has arisen to show that Placentals are descended from Marsupials, and of late, evidence has been coming in directly against this view. In fact zoo-palæontology now indicates that Marsupials and Placentals are parallel phyla, arising from a common stock, while Monotremes are so different that they may even be considered diphyletic, or derived independently from the Reptilia, as maintained by Mivart among others, and latterly by Seeley.

So far as major classification is affected by this conception, it appears therefore that we must revert to Gill's divisions of 1872, constituting only two sub-classes of Mammals, namely:

A—Eutheria	and B—Prototheria.
Marsupials, Pla-	Monotremes.
centals.	

Marsupials are less primitive than the placental Insectivores, and Marsupials and Placentals are certainly far nearer each other than either are to the Monotremes.

To guide our speculation in the unknown pre-Tertiary period, we may gather certain positive principles from the known evolution of the Tertiary mammalia. First, we know that *adaptive radiation*, characteristic of all vertebrates, and beautifully illustrated among Reptilia, is in a very high degree distinctive of Mammalia, because of their superior plasticity.<sup>+</sup>

\*Opening the discussion before the International Congress of Zoologists at Cambridge. (In conjunction with Professor H. G. Seeley.)

<sup>+</sup> We know nothing of Africa, whether it enjoyed a radiation of its own or borrowed its fauna from other continents.

There is the (I) Marsupial radiation of Australia (Meteutheria)\*---now passing its prime, then the (II) Tertiary Placental radiation of the Northern Hemisphere (Ceneutheria), and another quite independent (III) Tertiary placental radiation in South America, (rendered less pure in course of the Tertiary period by migration from I and II). IV, There is the entirely distinct and archæic Cretaceous Placental Radiation of the Northern Hemisphere (Meseutheria), which extends into the Tertiary, and may have given origin to II and III, although as yet we have no direct proof of it.

We mark the fact that the above radiations are all of *ordinal* rank, for the Marsupial radii, although termed families, are adaptively equivalent to several Placental orders.

If we apply these same principles to the Jurassic, we apparently have evidence of a more fundamental (V), Sub-class radiation of Placentals and Marsupials, and probably Monotremes, of world-wide distribution. (This involves a controverted question, to which I shall revert, for by some zoologists these animals of the Purbeck Clays, Como Beds, and Stonesfield Slates are considered exclusively Marsupials and Monotremes.) Finally far back in the Perm-Trias we certainly observe (VI), the Theromorph or Theriodont Reptilian radiation, spurs of which may have given rise to the Mammalia.

The focal-types, or most primitive forms of the radiations. I-IV, were certainly small, terrestrial, clawed, insectivorous or omnivorous forms. It is noteworthy that in the evolution of each radiation, so far as we know at present, land types and organs are invariably primitive, and water types and organs are secondary, exactly as we find it among the Reptilia. In fact we have not found a single instance in which a mammal or reptile series is known to be transforming from a water into a land type; it is always the reverse. There is certainly no evidence for a cetoid (Albrecht) stem of the Mammals. Again it is obvious that neither carnivorous nor herbivorous types with highly specialized or reduced teeth and feet can be so central as insectivorous and omnivorous types. In fact the Insectivores among Placentals, and Opossums among Marsupials, are the only animals which have preserved the dental prototype close to that of the Promammal.

The backward convergence of all Tertiary mammalia to a Creodont stem, as indicated in the chart, affords the clearest demonstration of the existence of an earlier insectivorous stem, and it not only accords with the above principles, but we are thus carried a step further to realize that the Creodont ancestor must have been a generalized Insectivore.

\*The Eutheria may embrace the Meteutheria or Marsupials, the Meseutheria or primitive Mesozoic Placentals, the Ceneutheria or Tertiary Placentals.

To reconstruct the ancestral Eutherian skeleton, therefore, we should divest the Creodonta and Insectivora, in their anatomy and development, of all their secondary specializations, and combine all their truly primitive characters. This ideal Eutherian is nearer the pro-Marsupial than we supposed; it has the following chief characters: Head large, body relatively small. Anterior nares terminal, face elongate. Insectivorous or omnivorous habit. Molar teeth pointed, tritubereular. Typical dental succession. Vertebræ with intercentra. Dorsolumbars not exceeding 20. Back arched, tail long and powerful. Scapula and ilium narrow, acuminate. Humerus with powerful



deltoid crest, condylar crests and entepicondylar foramen. Femur with three trochanters. Feet plantigrade. Centralia and tibiale. Fore-limb more or less prehensile, elbows everted.

Now the Creodonta are members of that Cretaceous radiation, IV, which we find in full bloom in the Basal Eocene, mingled with the dying group of Multituberculates, which belong to the Jurassic radiation, V. In the Mid—and Uppermost Jurassic (Stonesfield, Purbeck

In the Mid—and Uppermost Jurassic (Stonesfield, Purbeck and Como Beds) however, occur all three types, which theoretically constitute radiation V: first, the *Triconodonts* primitively but typically *Marsupial* in structure; second, the *Insectivora primitiva*, primitively *Placental* in type, insectivorous and without a single Marsupial character either in jaw or teeth; third, the *Multituberculata*, whose sub-class position is now assumed to be *Monotreme*. Always keeping in mind that our direct evidence here is of the most limited character, since we have neither skulls nor skeletons, only teeth and jaws, we are tempted to hypothetically connect the Creodonta with the Insectivora Primitiva, and to assume that there existed in the Mid-Jurassic, as above stated, the well advanced radiation V of the two sub-classes of EUTHERIA and PROTOTHERIA as defined by Gill.

The problem of the Origin of the Mammals now resolves itself into the connections between these two sub-classes either with the Reptilia or Amphibia, and we turn back to the three contemporary Upper Permian reptile groups:

1. *Pareiasauria or Cotylosauria*, land animals with a solid skull and replete with Stegocephalian or Amphibian characters, certainly the most primitive reptiles.

2. Proterosauria or Proganosauria, with an open two-arched skull, specialized reptiles, which have apparent affinities with the Crocodilia, Dinosauria, Rhyncocephalia and Squamata (Dolichosauria, Mosasauria, Lacertilia and Ophidia).

3. Theriodontia or Theromora (Dicynodontia, Cynodontia and Gomphodontia), with an open, single-arched, skull (as in the Chelonia, Plesiosauria, Icthyosauria and Mammalia).

The Theriodontia as perceived by Owen in 1876, and now fully confirmed by Seeley, are astoundingly mammalian in type. They are essentially quadrupedal, long-limbed, terrestrial reptiles, totally dissimilar from all other reptiles, and standing far away from them. They also present an advanced stage of functional radiation in tooth and skull structure in adaptation to carnivorous, omnivorous and herbivorous habits, to which, when known, their skeletons will probably be found to conform. The shoulder girdle is of Monotreme type; in other features of the skeleton they are strikingly like the ancestral Eutherian, described above. The skull may in fact be reduced to the Eutherian type by the coalescence of the prefrontals, postorbito-frontals and quadrates with the adjacent elements, and by the loss of the ectopterygoids or transverse The teeth are promammalian in formula, and pro-tribones. tubercular or multitubercular in form. The skeleton so far as known is partly Eutherian, partly Monotreme or Prototherian.

Two alternatives at this point present themselves: First: Are the Monotremes directly derived from such a type as these Theriodonts, leaving an independent derivation for the Eutherian or Marsupio-placental stock, as has been suggested by Seeley? Second: Must we set aside the Theriodonts for an Amphibian stem form on account of the numerous Amphibian resemblances which Hubrecht and others find in the development and anatomy of the lower Mammalia? The first question is now unanswerable, although at present the evidence that the Mammalia are diphyletic is certainly considerable. Second, the investigation of the placental ovum rises to extreme importance; if the Eutherian ovum is of Amphibian type, the Mammalia are certainly diphyletic, for the Monotreme ovum is certainly of reptilian type. This point may be met by supposing that at the time the Marsupio-placentals were given off, the Theriodontia conserved a number of Amphibian characters, which were at the time or subsequently lost.

The problem of most immediate concern, therefore, is whether the Theriodontia are actually the long-sought Promammalia of Hæckel, Hypotheria of Huxley or Sauromammalia of Baur, or whether they present a fresh instance of extensive parallelism due to the assumption of habits analogous to those of Mammalia. Professor Seeley has just presented the latter view,\* and it is certainly true that none of the known Theriodontia fill the characters outlined above as those we must look for in the Promammal or Eutherian stem, for they are all too large and too specialized.

There are however grounds for the more sanguine former view, that the Theriodontia are the Hypotheria or Promammalia, because it appears that within the order may well have existed some small insectivorous types, far less specialized in tooth structure than either the carnivorous Cynodonts or herbivorous Gomphodonts, as one of those conservative spurs of adaptive radiation which form the focus of a new progressive type.

The problem will therefore be settled by additional discovery and knowledge of the structure of the diverse types which undoubtedly composed this remarkable group.

Note. We can happily preserve that part of Huxley's speculation upon the origin of the Mammals which pictured the Insectivora as nearest the ancestral type. The Amphibian (or Stegocephalian) origin of the Mammalia which he defended, is wholly set aside, if the view here taken is correct, for the Theriodontia are certainly not Amphibia in any sense.

\* "Anomodonts are not the parents of Mammals, but a collateral and closely related group. The common parent of both may be sought in rocks older than Permian, perhaps in Silurian or Devonian strata." Printed abstract of Professor Seeley's argument, p. 3.

# ART. XII.—On the Chemical Composition of Tourmaline; by S. L. PENFIELD and H. W. FOOTE.

INTRODUCTION AND HISTORICAL.-There is probably no common mineral whose chemical composition has proved more perplexing and been so little understood as tourmaline. Some reasons for this are, first, that the mineral presents certain peculiarities in chemical composition of an unusual nature; second, the analysis of tourmaline has been one of the difficult problems of analytical chemistry, hence reliable data for the calculation of the formula have not been easily obtained; and, lastly, although good analyses have been made, the results have not been thoroughly relied upon, nor have they been interpreted to the best advantage. The present investigation was undertaken, therefore, with the hope that by making a few analyses with the utmost possible care on tourmalines of exceptional purity, it would be possible to find a satisfactory explanation of the chemical composition of this interesting mineral.

In order to appreciate the problem in hand, it will be necessary to review briefly the work and the results of previous investigators.

The analyses of Vauquelin and Klaproth, made in the early part of this century, were naturally defective, because at the time they were made, lithium was unknown, it had not been discovered that tourmaline contained boron, and analytical methods were not perfected.

In 1818 the presence of boron was detected by Lampardius,\* and in the same year Arfvedson<sup>+</sup> discovered the new alkali metal lithium, and showed its presence in spodumene, petalite and tourmaline.

In 1827 Gmelin<sup>†</sup> published analyses of ten varieties of tourmaline, but his results led to no satisfactory formula, although the essential constituents of the mineral, with the exception of the boric oxide, were determined with a considerable degree of accuracy.

In 1845 Hermann<sup>§</sup> published the results of four analyses of tourmaline from Russian localities. He proved conclusively that the iron was ferrous, and not ferric as considered by previous investigators. Boric oxide was not directly determined, but estimated by difference, and the results compare favorably with the direct determinations made by our present methods.

- + Schweiger's Jour. d. Chem. u. Phys., xxii, p. 111.
- ‡ Pogg. Ann., ix, p. 127. § Journal für prakt. Chem., xxxv, p. 232.
- AM. JOUR. SCI.-FOURTH SERIES, VOL. VII, NO. 38.-FEBRUARY, 1899.

<sup>\*</sup> Ann. d. Phys. u. Chem., xxx, p. 107.

He was the first to point out that silica and boric oxide are present in the definite molecular proportion 4:1. He erroneously decided that tourmaline contained carbon dioxide, the reasons being as follows: It was generally believed at that time that the mineral contained no water, as stated by Hermann "die Turmaline keine Spur davon enthalten." and it is true that when fragments are tested by the usual method of heating to redness in a closed tube no water is obtained. It is only when the material is heated intensely, best as fine powder, that hydroxyl is decomposed and water given off. When Hermann dissolved fragments in a borax bead he observed that a gas was evolved, and, since it was believed that this could not be water vapor, he supposed that it must be carbon dioxide. Pains were taken to fuse some of the mineral in a tube with borax, and to conduct the gas into lime water, by which treatment a precipitate was obtained which effervesced with acids, but it is safe to assume that the carbon dioxide thus detected was derived from improperly purified air and not from the mineral.

In 1850 Rammelsberg\* published the results of the analyses of thirty varieties of tourmaline. The execution of such a large number of analyses must be regarded as a very great undertaking, since at that time gas and many facilities of our modern laboratories were not available, and many methods of analysis were not perfected. Special evidence is given that great care was taken in the selection of material for analysis and in the analytical methods, which appear to have been well chosen and reliable in character. The analyses, however, were defective in several important particulars. Thus the iron was regarded chiefly as ferric. Believing, like Hermann, that tourmaline contained no water, and having detected the presence of fluorine in some varieties of the mineral, he supposed that the considerable loss on ignition which occurred was due to the volatilization of silicon fluoride, and from this loss he estimated fluorine to be present in amounts varying from 1.30 to 2.51 per cent. Direct determinations of boric oxide were made in three cases only, and in the remaining analyses this important constituent was estimated by difference. Although the analyses led to no satisfactory formula, they indicated certain prominent characteristics of the mineral, namely, the great variation in the relative amounts of aluminium, iron, magnesium and alkalies, and the nearly uniform amounts of silica and boric oxide.

Fully realizing certain defects in his earlier analyses, Rammelsberg<sup>+</sup> published in 1870 a revision of his former paper.

\* Ann. der Phys. u. Chem., lxxx, p. 449 and lxxxi, p. 1.

+ Ann. der Phys. u. Chem., ccxv, pp. 379 and 547.

At this time it was shown that all varieties of tourmaline contained chemically combined water, and the amount of water was estimated from the earlier determinations of the loss on ignition after making certain corrections for volatilization of silicon fluoride. He found that the iron was chiefly if not wholly ferrous, and recalculated accordingly his earlier results. Six direct determinations of boric oxide were made, and it is pointed out that these amounts correspond closely with the indirect determinations by difference. As a result of the revision, Rammelsberg reached the conclusion that all tourmalines are derived from the acid  $H_eSiO_e$ . In this he considered the hydrogen atoms to be replaced by metals of different valences, or, in other words, he regarded tourmaline as composed of a mixture of the following molecules:

Furthermore he decided that certain varieties correspond closely to the special formulas

 $I. \begin{cases} R'_{_{3}}Al_{_{2}}BSi_{_{9}}O_{_{10}} \\ R''_{_{9}}Al_{_{4}}B_{_{9}}Si_{_{4}}O_{_{20}} \end{cases} \text{ and } II. \begin{cases} R'_{_{6}}Al_{_{12}}B_{_{4}}Si_{_{9}}O_{_{45}} \\ R''_{_{3}}Al_{_{12}}B_{_{4}}Si_{_{9}}O_{_{45}} \end{cases}$ 

while he regarded others as mixtures of these two molecules. By substituting hydrogen atoms for the metals and boron of these special formulas, the acids become respectively  $H_{s4}Si_4O_{s0}$  and  $H_{s4}Si_9O_{s0}$ , both of which are multiples of  $H_cSiO_s$ . He concluded that the SiO<sub>2</sub> and  $B_sO_3$  are not present in a definite molecular proportion, but that boron plays the part of a metal and is isomorphous with aluminium.

In 1888 Riggs<sup>\*</sup> published the results of twenty analyses of various types of tournaline from American localities. The analyses were executed in the laboratory of the U. S. Geological Survey at Washington, and bear every evidence of being made with the precision and care characteristic of the analytical work of that laboratory. Borie oxide, water and ferrous oxide were determined directly by reliable methods, and a high degree of accuracy is claimed for the analyses. A careful description of the quality of the material analyzed is not given, and although it is to be supposed that great care was taken in its selection, the following statement has left this in doubt: "The analyses do not represent ideal compounds, but are made of material more or less impure . . . . " Riggs concludes that the analyses give "as a general tournaline formula the simple boro-orthosilicate R, BO, 2SiO, " which is expressed graphically as follows:

<sup>\*</sup> This Journal, III, xxxv, p. 35.

He supposes R to include H, Li, Na, K, Ca, Mg, Fe, Al and small amounts of the Al-O or possibly Al-OH radicals. It may here be stated that the foregoing formula is identical in type with the special formula  $R'_{a}Al_{a}BSi_{a}O_{io}$  (H<sub>a</sub>BSi<sub>a</sub>O<sub>io</sub>) of Rammelsberg, and considering boron as replacing hydrogen like a metal the silicic acid from which the formula is derived becomes  $H_{ia}Si_{a}O_{io}$  or  $H_{a}SiO_{a}$ . Riggs further states that, owing to slight variations, the ratios give nearly the "equally simple general formula  $R_{io}BO_{a}2SiO_{a}$ " stating that "between these two views there are at present no means at hand of deciding." It would seem, however, that the last formula is impossible, for, considering hydrogen atoms as replacing  $R_{io}$ , the acid can not be split up like other oxygen acids into silicic and boracic anhydrides and water. There are also given the following special formulas for three pronounced types of tourmaline:

I.	Lithia tour.	12SiO,, 3	3B.O.,	4H <sub>0</sub> ,	8Al_O_,	2(NaLi)	"O.
II.	Iron tour.	12SiO,	3B,0,,	4H_0,	7Al 0,	4FeO, ´	Na <sub>o</sub> O.
III.	Mg tour.	12SiO <sub>2</sub> ,	$3B_2O_3$ ,	$4H_{2}O,$	5 Al <sub>2</sub> O <sub>3</sub> ,	<sup>28</sup> / <sub>3</sub> MgO,	$\frac{2}{3}$ Na <sub>2</sub> O.

By substituting hydrogen atoms for the metals in these special formulas we obtain :

I. and II. 
$$H_{60}B_{6}Si_{12}O_{62}$$
 or  $H_{20}B_{2}Si_{4}O_{21}$ .  
III.  $H_{58}B_{6}Si_{12}O_{62}$  or  $H_{10\frac{1}{4}}B_{2}Si_{4}O_{20\frac{1}{4}}$ .

Soon after the appearance of Riggs' article, Wülfing\* recalculated the results of these twenty analyses and concluded that all tourmalines may be regarded as isomorphous mixtures of two aluminium silicates, "Alumosilicate," of the following composition.

I. Alkali tourmaline  $12SiO_{2}$ ,  $3B_{2}O_{3}$ ,  $8Al_{2}O_{3}$ ,  $2Na_{2}O_{2}$ ,  $4H_{2}O_{3}$ , II. Magnesia tourmaline  $12SiO_{2}$ ,  $3B_{2}O_{3}$ ,  $5Al_{2}O_{3}$ , 12MgO,  $3H_{2}O$ .

In these formulas it is assumed that the isomorphous elements K and Li replace the Na; Fe''' the Al; and Fe'', Mn and Ca the Mg. By substituting hydrogen atoms for the metals in the foregoing formulas it is found that they both are derivatives of the same acid,  $H_{so}B_sSi_1O_{so}$ , or  $H_{so}B_sSi_4O_{si}$ . The conclusions derived by Wülfing are that, although in most cases the results of the analyses agree with the percentage values calculated from his formulas, the agreement is not always satisfactory. This he ascribes to the possible need of a

\* Mineralogische und petrographische Mittheilungen, x, p. 161.

third formula; to possible inaccuracies in the difficult ferrous iron determinations; and in part to the fact, as stated by Riggs, that "the analyses do not represent ideal compounds. . . ." He therefore considers it necessary that further analyses of more carefully selected material should be made.

At about this time also Scharizer\* published analyses of three varieties of tourmaline from Schüttenhofen, Bohemia, and discussed his results in connection with the analyses of Riggs. His final conclusion is that, with the exception of the green varieties, tourmalines possess a chemical constitution which can be expressed by the general formula

$$\begin{bmatrix} I & II \\ R_2 R \end{bmatrix}_2 \begin{bmatrix} II & III \\ R_3 R_2 \end{bmatrix}_4 Al_s (SiO_s)_{12} \begin{bmatrix} O \\ (BO, HO, F)_2 \end{bmatrix}_7.$$

This formula is certainly difficult to comprehend, and, if we understand it correctly, the univalent radicals BO and HO are isomorphous with fluorine, and these constituents, taken twice, can replace oxygen.

In 1889 Jannasch and Kalb<sup>+</sup> published the results of nine tourmaline analyses, in which the water and boron were determined directly. These investigators derived from their analyses the general formula R<sub>9</sub>. BO<sub>2</sub>. (SiO<sub>4</sub>)<sub>2</sub>, for which the following structural formula was proposed :



This formula,  $R_{\circ}$ . BO<sub>2</sub>. (SiO<sub>4</sub>)<sub>2</sub>, is identical with the one proposed by Riggs, and essentially like the special formula  $R'_{4}Al_{2}BSi_{2}O_{10}$  of Rammelsberg. The following special formulas are also given :

These special formulas in their general type are similar to those proposed by Riggs. By substituting hydrogen atoms for the metals they all reduce to one and the same acid,  $H_{120}B_{12}Si_{24}O_{122}$  or  $H_{29}B_{2}Si_{4}O_{21}$ .

\* Zeitschr. für Kryst., xv, p. 343.

+ Berichte der deutschen chemischen Gesellschaft, vol. xxii, p. 216. Also Inaugural Dissertation, Geo. W. Kalb, Göttingen.

# 102 Penfield and Foote-Composition of Tourmaline.

There is evidence that Jannasch does not place great confidence in the foregoing formulas, for in Hintze's Mineralogy\* the composition is expressed as follows:

Ι.	Lithia tourmaline	Si, O <sub>a</sub> B <sub>a</sub> Al <sub>i</sub> (Na, Li) <sub>4</sub> H <sub>a</sub>
II.	Iron tourmaline	Si, O at B Al, Fe Na H,
тт	35 1	O' O THAL ME AT TT

III. Magnesia tourmaline Si<sub>12</sub>O<sub>69</sub>B<sub>6</sub>Al<sub>13</sub>Mg<sub>12</sub>Na<sub>2</sub>H<sub>7</sub>

These formulas are essentially different from the ones first proposed, which may readily be seen by substituting hydrogen atoms for the metals and comparing the resulting acids, as follows:

 $\begin{array}{c} I. \ H_{ab}B_{e}Si_{1}O_{e3} \ \ or \ \ H_{1s}B_{2}B_{2}Si_{4}O_{21} \\ II. \ \ H_{ab}B_{2}Si_{1}O_{e7} \ \ or \ \ H_{2s}B_{2}Si_{4}O_{22} \\ III. \ \ H_{-2}B_{2}S_{12}O_{e6} \ \ or \ \ H_{24}B_{2}Si_{4}O_{22} \end{array}$ 

Soon after the appearance of the articles of Riggs and of Jannasch and Kalb, the results of their analyses were recalculated by Goldschmidt,<sup>+</sup> and the conclusion was reached that tourmaline may be regarded as containing the two following molecules:

> I. Alkali tourmaline  $R'_{20}R''_{24}R''_{44}Si_{31}O_{162}$ II. Magnesia tourmaline  $R'_{20}R''_{24}R''_{44}Si_{31}O_{162}$

These formulas are both derived from an acid  $H_{200}Si_{31}O_{162}$  or  $H_{4.46}SiO_{5.22}$ .

In 1893 Rheineck,  $\ddagger$  after calculating the results of the many tourmaline analyses, concluded that the composition of all tourmalines may be expressed by formulas of the following type, in which Al<sub>4</sub> appears as a constant:

I.	Alkali tourmaline	Al <sub>s</sub> Si <sub>3</sub> BH <sub>3</sub> O <sub>15</sub>	
II.	Alkali tourmaline	Al <sub>s</sub> Si <sub>3</sub> B <sub>2</sub> H <sub>2</sub> O <sub>15</sub>	

III. Magnesia tourmaline Al<sub>4</sub>Si<sub>5</sub>B<sub>2</sub>M<sub>4</sub>H<sub>4</sub>O<sub>25</sub>, etc.

M represents the bivalent metals Fe, Mn, Mg and Ca. H includes Na, Li and K. Among the numerous examples he stated that the composition of the black tourmaline from Pierrepont, N. Y., may be represented by either of the following expressions:

$ \begin{cases} 114  Al_{4}Si_{5}B_{2}M_{4}H_{4}O_{25} \\ 10  Al_{4}Si_{3}B_{6}O_{25} \end{cases} \text{ or } \begin{cases} 2 \\ 2 \\ 2 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\$	10 Al_Si_B_H_ $O_{18}$ 93 Al_Si_B_M_4H_ $O_{25}$ 21 Al_Si_B_M_ $O_{26}$
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\* Vol. ii, p. 311 (communication from manuscript by Jannasch).
† Zeitschr. für Kryst, xvii, pp. 52 and 61.
‡ Zeitschr. für Kryst., xxii, p. 52.

By substituting hydrogen atoms for the metals in these expressions, and multiplying by the factors, 114 and 10 in the one case, and 10, 93 and 21 in the other, the acids become  $H_{ace}B_{ace}S_{ace}O_{ace}$  and  $H_{ace}B_{ace}S_{ace}O_{ace}$ , or, when simplified,  $H_{ace}B_{ace}S_{ace}O_{ace}$  and  $H_{ace}B_{ace}S_{ace}O_{ace}$ . The improbable nature of such acids is evident. In the opening paragraph of his article Rheineck stated that the obscure and complex chemical relations of this mineral have necessitated a series of speculations and calculations extending somewhat interruptedly over a period of many years, in order to arrive at results such as those embodied in the foregoing formulas.

In 1895 Clarke\* discussed the constitution of tourmaline and proposed the following formulas :

1.	2.
$ \begin{array}{c} \mathbf{\hat{SiO}_4 \equiv R'_s} \\ \mathbf{Al-SiO_4 \equiv Al} \\ \mathbf{\hat{SiO}_4 = Al-BO_2} \end{array} $	$SiO_{4} \equiv MgH$ Al-SiO_{4} = MgH SiO_{4} = Al-BO_{4}
Ål-BO <sub>3</sub> =NaH	Al_BO <sub>3</sub> =NaH
$siO_4 = Al - BO_2$ Al-SiO_4 = Al SiO_4 = Al	$Al = SiO_4 = Al = BO_2$ $Al = SiO_4 = Al$ $SiO_4 = Al$
3.	4.
$SiO_4 \equiv MgH$ Al-SiO_4 $\equiv MgH$ $SiO_4 = Al - BO_2$	$SiO_{4} = MgH$ Al-SiO_{4} = MgH $SiO_{4} = Al - BO_{2}$
Al-BO <sub>3</sub> =NaH	Al-BO <sub>s</sub> =NaH
$Al-SiO_4 = Al - BO_2$ $Al-SiO_4 = MgH$ $SiO_4 = Al$	$\mathrm{SiO}_{4} = \mathrm{Al} - \mathrm{BO}_{2}$ $\mathrm{Al} - \mathrm{SiO}_{4} \equiv \mathrm{MgH}$ $\mathrm{SiO}_{4} \equiv \mathrm{MgH}$

Clarke assumes variations from these formulas in that Fe''' and Cr can replace the Al; Fe'' and Mn the Mg; Ca the NaH; and small amounts of F the BO<sub>2</sub>. Proof of a constitution corresponding to the formulas cannot of course be expected, but it is doubtful whether aluminium could exercise such varied functions as the formulas indicate. The grounds for believing that fluorine can replace BO<sub>2</sub> are not stated. The acid from which all these formulas are derived is  $H_{20}B_3Si_4O_{202}$ .

Lastly Groth<sup>†</sup> has adopted the formula of Jannasch [SiO<sub>1</sub>], BO<sub>2</sub>, R'<sub>2</sub>, but interprets it as follows:

\* Bulletin of the U. S. Geological Survey, No. 125, p. 56.

† Tabellarische Uebersicht der Mineralien, 4te Auflage, 1898, p. 117.



or [SiO4]2[AlO. BO]([AlO]2, Mg, Fe, Na2, Li2, H2)

That the univalent radical [AlO] can replace  $\mathbf{R}'$  does not appear in the original article of Jannasch, and it makes a decided difference whether three R's are replaced by one atom of Al or by three [AlO] radicals. The latter assumption implies a basic character which tourmaline does not possess.

We have thus reviewed the work already done in order to show the difficulties which this problem has presented. It is, however, interesting to note how closely different investigators come to one type of acid from which all varieties of tourmaline are derived. For the sake of comparison these acids have been reduced to four silicon atoms, and are given below, both as borosilicic acids and with the boron replaced by hydrogen.

Rammelsberg	$\begin{cases} H_{18}B_{2}Si_{4}O_{20}\\ H_{10}B_{10}Si_{10}O_{10} \end{cases}$	or or	$H_{24}Si_4O_{20} = H_6SiO_6$ $H_2Si_4O_2$
	$(H_{18}B_{6}Si_{4}O_{60})$	or	$H_{a4}Si_4O_{a2}$
Rigge	$H_{20}B_{2}Si_{4}O_{20}$	or	$H_{26}^{*}Si_{4}O_{20}^{*}$ (Irrational)
rugge	$H_{20}B_{2}Si_{4}O_{21}$	or	$H_{26}Si_4O_{21}$
	$(H_{19\cdot33}B_{2}Si_{4}O_{20\cdot66})$	or	H <sub>25-33</sub> Si <sub>4</sub> O <sub>20-66</sub>
Isamasah and Kally	(H.B.SiO	or	H <sub>24</sub> Si <sub>4</sub> O <sub>21</sub>
Jannasen and Kato	II B Si O	or	$H_{26}^{*}Si_{4}O_{20}^{*}$
Wülfing	H <sub>20</sub> B <sub>2</sub> Si <sub>4</sub> O <sub>21</sub>	or	$H_{26}Si_4O_{21}$
Goldschmidt			H <sub>25-8</sub> Si <sub>4</sub> O <sub>20-9</sub>
Dhaina ala	H. B. Si O	or	H <sub>ass</sub> Si <sub>1</sub> O <sub>nes</sub> (Irrational)
Memeek	$H_{18,9}B_{1,9}Si_4O_{20,3}$	or	$H_{24+6} Si_4 O_{20+3}$ etc.
Clarke	H <sub>19.33</sub> B <sub>2</sub> Si <sub>4</sub> O <sub>20.66</sub>	or	H <sub>25.33</sub> Si <sub>4</sub> O <sub>20.66</sub>
	NEW ANALYS	ES.	

Method of analysis.—The present investigation was undertaken with the expectation that for the solution of the problem in hand it would probably not be necessary to make a long series of analyses but rather exceedingly accurate analyses of a few carefully selected types of tournaline. We therefore prefaced our work by a careful study of those features of the tournaline analysis, which have proved most difficult. The method proposed by Gooch\* of distilling off the boron with methyl alcohol and weighing it as calcium borate is very exact,

\* Amer. Chem, Jour., ix, p. 23.

but its application to an insoluble silicate, especially one containing fluorine, needed careful study. Mixtures were accordingly made of silicates to which weighed quantities of borax and fluorite were added and the following conditions were determined, which yielded the most accurate boron determina-The mineral was fused with from four to five parts of tions. sodium carbonate, the fusion extracted with water, and, without filtering, an excess of ammonium carbonate was added. The insoluble residue and the precipitate were filtered off, the filtrate concentrated, acidified slightly with nitric acid and distilled with methyl alcohol. The residue from the sodium carbonate fusion together with the precipitate produced by the ammonium carbonate was fused again with sodium carbonate, treated with water, filtered and distilled with methyl alcohol after acidifying with nitric acid. About one half of one per cent of boric oxide was obtained from the second treatment, and in no case did we succeed in obtaining an exact determination of the boric oxide without repeating the fusion. The weighed mixture of calcium borate and oxide was in all cases found to contain a small amount of fluorine. It was therefore dissolved in hydrochloric acid, and part of the lime together with calcium fluoride was precipitated with sodium carbonate. The precipitate was ignited, treated with acetic acid and the resulting calcium fluoride weighed. The amount of fluorine thus found never amounted to over 0.20 per cent.

Fluorine was determined by the modified Berzelius method described by Penfield and Minor.\*

Water was determined by fusing the mineral with sodium carbonate in a combustion tube and collecting the water in a weighed tube containing sulphuric acid, a method which has been thoroughly tested and is known to give reliable results.<sup>+</sup>

For the determination of the bases the mineral was decomposed by fusion with sodium carbonate and the silica separated as usual. It was found by experiment that the amount of silica volatilized by the small amount of fluorine in the mineral could practically be neglected. In one variety of tournaline two determinations of silica made by the Berzelius method of fusing the mineral and a weighed amount of silica with sodium carbonate, and separating the silica with ammonium carbonate and an ammoniacal solution of zinc oxide, gave 36.69 and 36.76 per cent, while determinations by the ordinary method gave 36.75 and 36.73 per cent. A similar conclusion, that when the amount of fluorine is small it is not necessary to separate the silica by the Berzelius method, was also reached by Riggs.

> \* This Journal, III, xlvii. 1894, p 387. † This Journal, III, xlviii. 1894, p. 31.

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The filtrate from the silica was evaporated to dryness, moistened with hydrochloric acid and repeatedly evaporated with methyl alcohol to remove all possibilities of boric oxide being precipitated with the bases and thus increasing their weight.

For the determination of the alkalies the Smith fusion was employed and, after removal of animonium salts, the residue was treated with acid and methyl alcohol and evaporated to remove any borate that might possibly be present. Lithium was separated by the Gooch method of boiling with amyl alcohol,\* and was finally weighed as sulphate.

It was proved by careful qualitative tests  $\dagger$  that the iron was ferrous, and that, at the most, not more than traces of ferric iron could be present. This statement holds good not only for the varieties analyzed, but for all the varieties of black tourmaline which were accessible to us.

Selection and preparation of material.—One of the varieties selected for analysis was the white or colorless tourmaline from De Kalb, St. Lawrence Co., New York. This was chosen because according to the analysis of Riggs it represented almost the extreme type of a magnesia tourmaline, and, containing almost no iron, there could be no appreciable error from a failure to estimate that constituent correctly. The material was derived in part from a specimen in the Brush Collection and in part from specimens collected by one of us (Penfield) while connected with the U. S. Geological Survey. The clear, colorless, glassy material was most carefully selected with the aid of a lens, ground and sifted to a uniform grain, and suspended in methylene iodide. The specific gravity was uniform, and the portion used for the analysis floated at 3.065 and sank at 3.033. As an additional precaution the grains were treated with a mixture of hydrochloric and hydrofluoric acids, which have almost no action even on finely pulverized tourmaline, in order to remove any possible traces of adhering calcite, tremolite or pyroxene, although these were not seen nor believed to be present. It may be stated concerning the final product that probably it was as pure as it is possible to get a mineral substance.

Another variety selected for analysis was from the feldspar quarries at Haddam Neck on the Connecticut River. Wonderful tourmalines have recently been obtained from this locality, and they are already well know to most collectors. We are indebted for our supply of material to Mr. Ernest Schernikow of New York, who generously placed at our disposal an almost unlimited supply of crystals of gem quality. We selected small prisms, 2 to 4<sup>mm</sup> in diameter, of a uniform rather pale green color. They were of ideal purity, perfectly transparent

and without flaws. Any traces of foreign material that might possibly be adhering to their outer surfaces were removed by treating them for a considerable time with hydrofluoric acid. The specific gravity, taken with the chemical balance, was found to be 3.089.

We were prepared to extend our investigation by analyzing other varieties, but having completed the above mentioned two and finding that the results corresponded with those of other investigators, it was decided that the data which would be derived from further analyses would probably add very little to the knowledge which we already possess.

The results of the analyses are as follows :

# Colorless Tourmaline, DE Kalb, N. Y.

	001	010000	roomanny Du	There are a marked and a marked			
	I.	II.	Average.				Riggs.
SiO,	6.69	36.76	$36.72 \div 60 =$		612	4.00	36.88
TiO,	•06	•05	•05				.12
B <sub>0</sub> ,1	0.86	10.77	$10.81 \div 70 =$		$\cdot 154$	1.01	10.58
Al <sub>2</sub> O <sub>3</sub> 2	9.75	29.61	$29.68 \div 17 = 1$	( 1.741			28.87
FeO	·23	·21	$22 \div 36 =$	·006			.52
MgO1	4.91	14.92	$14.92 \div 20 =$	.746			14.53
CaO	3.47	3.20	$3.49 \div 28 =$	·125 }	3.042	19.90	3.70
Na <sub>.</sub> O	1.29	1.23	$1.26 \div 31 =$	·040			1.39
K <sub>2</sub> Ó	•07	•03	$05 \div 47 =$	.002			·18
Н.О	2.98		$2.98 \div 9 =$	•331			3.56
F	•92	•95	·93÷19=	·049 )			•50
						-	

101.11

O equivalent to F....

100.72

·39

·21

100.83

GREEN TOURMALINE, HADDAM NECK, CONN.

						Drazn.
I.	II.	Average.				Riggs.
SiO	37.05	$36.96 \div 60$	=	·616	4.00	37.39
TiO <sub>2</sub> •03	.03	.03				2 ·
$B_{2}O_{3}$	10.92	$11.00 \div 70$	=	·157	1.02	10.29
Al.O 39.53	39.59	$39.56 \div 17$	=2.327	)		39.65
FeO 2.12	2.15	$2.14 \div 36$	<b>=</b> .059	i		*2.42
MnO 1.96	2.04	$2.00 \div 35$	5 = .056			1.47
MgO 15	·15	·15÷20	= .008			none
CaO 1.32	1.25	$1.28 \div 28$	= .046	> 3.078	19.98	•49
Na <sub>2</sub> O 2.13	2.06	$2.10 \div 31$	<b>=</b> .068	Ì		12.67
Li,Ö 1.65	1.63	$1.64 \div 15$	= .110			1.71
H <sub>0</sub> 3.14	3.06	$3.10 \div 9$	$= \cdot 344$			3 63
F 1.09	1.17	$1.13 \div 19$	<b>=</b> .060	j		•32
		101.09				100.04
O equivalent to	F	•48				.13
		100.61				99.91

\* Includes 0.15 per cent. Fe<sub>2</sub>O<sub>3</sub>.

↓ Includes 0.25 per cent. K<sub>2</sub>O.

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On treating the analyses according to the customary method of deriving a formula (dividing each constituent by its molecular weight and finding the ratio of the quotients) it was found that although the  $SiO_2$  and  $B_2O_3$ , were present in the proportion of 4:1, no definite relation could be detected between the silica, the different kinds of oxides, and the water. It was decided, therefore, to determine the relative number of hydrogen atoms equivalent to the metals and thus learn the acid from which tourmaline is derived. This was readily accomplished by dividing the constituents by appropriate fractions of their molecular weights; for example, since the aluminium atoms in Al<sub>2</sub>O<sub>3</sub> replace six hydrogens, the quantity of Al<sub>2</sub>O, was divided by one-sixth of its molecular weight, the FeO by one half of its molecular weight, etc. Since fluorine is regarded as playing the same role as hydroxyl, its ratio was added directly to that of the hydrogen. The result of this treatment is very satisfactory. The first analysis gives the ratio of SiO<sub>2</sub>:  $B_2O_3$ : H=4:1:19:90, and the second 4:1:02:19.98. Both ratios approximate so closely to 4:1:20 that there can be no reasonable doubt that the acid from which these tourmalines are derived is  $H_{20}B_2Si_4O_{21}$ . This formula may seem at first somewhat complex, but it is not especially so for a boro-silicic acid. It can not be simplified by division, and it is based upon the very best kind of evidence, namely, the close approximation to rational numbers of the two ratios, which are derived from widely separated types of tourmaline.

Before discussing the possible constitution of this acid, it will be shown to what extent the analyses of other investigators confirm the results obtained by us.

REVIEW OF RAMMELSBERG'S ANALYSES.—The analyses appear with certain variations in his different publications, and the results which will be discussed here are given in his *Mineralchemie*, 1875. These are quoted in the sixth edition of Dana's Mineralogy, and where there is occasion to refer to individual analyses they will be designated by the numbers assigned to them in the latter work. The same plan also will be adopted for the analyses of Riggs, Jannasch and Kalb and others. Thirty-five analyses are given by Rammelsberg, of which No. 34 is not complete.

Adopting the same method of calculation as applied to our own analyses, and using one-fourth of the silica as unity, the ratios of SiO<sub>2</sub>: B<sub>2</sub>O<sub>3</sub> were found to vary between 4:1.21 and 4:0.71, and the ratios of SiO<sub>2</sub> to the total hydrogen atoms between 4:16.5 and 4:19.7. The result of grouping the ratios of the hydrogen atoms is as follows:

Limits of variation, 16.5-17.5 17.5-18.5 18.5-19.5 19.5-19.7 Number of analyses, 8 12 12 2 The ratios of SiO<sub>2</sub> to the total hydrogen atoms show a wide variation, and the hydrogens for the most part fall far below 20, which is required by the new formula. Rammelsberg, however, claims that boron plays the part of a metal, replacing aluminium, and that all tourmalines are derivatives of an acid  $H_sSiO_5$  or  $H_{a_1}Si_4O_{a_2}$ . Replacing, therefore, the boron by hydrogens  $(B_2O_4)$  is equivalent to  $3H_2O_1$ , it is found that the ratios of SiO\_4 to the total hydrogens then vary from 4:21.9 to 4:25.1. The result of grouping the ratios is as follows:

Limits of variation, 21'9-22'5 22'5-23'5 23'5-24'5 24'5-25'1 Number of analyses, 3 10 17 4

The ratio of SiO, to the total hydrogens demanded by Rammelsberg's formula is 4:24, and in only seventeen, or onehalf, of the analyses are the ratios  $24 \pm 0.5$ , while they are reasonably sharp,  $24 \pm 0.2$ , in only seven cases. It would seem therefore that owing to certain defects the analyses fail to give decisive results. The ratios do not satisfactorily support Rammelsberg's formula nor the one which we have proposed. In his latest publications\* Rammelsberg claims great accuracy both for his analyses and for the analytical methods which he employed, and in justice to him it does not seem right to ignore his results without endeavoring to discover the possible defects of the analyses and the influences exerted by them upon the ratios. In the first place, it is believed, for the following reasons, that his silica determinations are too high: it is presumable that facilities were not at hand for producing the intense heat necessary for expelling the last traces of water from the silica; there is no statement that the silica was tested as to its purity by volatilization with hydrofluoric acid; and, lastly, a little silica might have been derived from glass beakers and even from the distilled water, provided it was kept in glass bottles or carboys. It is certain that the water determinations are too low, and this is admitted by Rammelsberg. It is well known that when a silicate containing fluorine and hydroxyl is heated some hydrofluoric acid is liberated, and if the experiment is tried in a closed tube the glass is etched, while probably the mineral also is attacked with the formation of silicon fluoride. Rammelsberg, + however, points out that only a portion of the fluorine is thus expelled, and since the amount of fluorine in tourmaline is small, the loss on ignition should give a fair estimate of the amount of water which the mineral contains. Loss on ignition seems to have been very carefully determined by Rammelsberg, and in those analyses in which

<sup>\*</sup> Berlin Akademie, 1890. Mineralchemie, Zweites Supplement, 1895.

<sup>†</sup> Mineral Chemie, Zweites Supplement, p. 284.

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fluorine is estimated the water is given as equal to the loss on ignition less either the fluorine or the silicon fluoride equivalent to it, while when no fluorine was determined a quantity is assumed, usually one-third to one-half of one per cent, and this quantity or the silicon fluoride equivalent to it is deducted from the loss on ignition. In the latter case the assumed quantity of fluorine never appears in the results as a constituent of the mineral. Again, no account seems to have been taken of the fact that on prolonged ignition the ferrous iron may become oxidized to ferric, thus causing the water deter-minations to be too low. In this connection it is interesting to refer to some results obtained by Riggs, who has given with many of his analyses both the loss on ignition and the direct water determinations. When much ferrous oxide is present the loss on ignition is less than the water, but when this loss is increased by an amount equivalent to the oxygen which the iron present can take up in changing from ferrous to ferric oxide, the results become almost equal. The results, in fact, would almost do for duplicate determinations, as shown below:

 $4\cdot 38 \ \ 4\cdot 16 \ \ 4\cdot 24 \ \ 3\cdot 97 \ \ 4\cdot 03 \ \ 3\cdot 64 \ \ 3\cdot 75 \ \ 3\cdot 71 \ \ 3\cdot 73 \ \ 3\cdot 82 \ \ 3\cdot 77 \ \ 3\cdot 60 \ \ 4\cdot 01$ 

 $\rm H_{2}O$  direct \_\_\_\_4'26 3'90 4'16 3'64 3'49 3'69 3'62 3'49 3'62 3'63 3'60 3'34 3'79

We cannot agree with Rammelsberg that the method adopted by Riggs for determining water directly gives too high results, for it has been abundantly proved that when properly executed it gives exceedingly accurate ones. It is safe to assume, therefore, that if the determinations of the loss on ignition as given by Rammelsberg are corrected for the oxidation of the iron, the results will furnish fair estimates of the percentages of water.

Accepting as an established fact that SiO<sub>2</sub> and B<sub>4</sub>O<sub>5</sub> are always present in tourmaline in the proportion 4 :1, Rammelsberg's results may be modified by correcting the water determinations and estimating both SiO<sub>2</sub> and B<sub>4</sub>O<sub>5</sub> by difference, thus distributing the errors of analyses upon two constituents, rather than upon the B<sub>2</sub>O<sub>5</sub> alone. Below are given the results of applying this method of correction to seven of Rammelsberg's analyses made upon varieties of tourmaline which have subsequently been investigated by either Riggs or Jannasch and Kalb. There are also given for comparison the analyses of the other investigators and Rammelsberg's figures for SiO<sub>4</sub>, H<sub>4</sub>O and loss on ignition.

	0	douverne	eur, N.Y.,	Monroe	, Conn.,	Haddar	n, Conn.,	Snarum,		
				Brow	nish-					
		Bi	own.	Bla	ick.	Bla	ack.	Black.		
		Rm. 1.	Rgs. 53.*	Rm. 7.	Rgs. 51.	Rm. 11.	Rgs. 47.	Rm. 12. J	. & C. 56.	
	TiO2		1.19		1.61		.57		1.10	
ed.	( SiO2	[35.76]	37.39	[36.40]	36.41	[34.75]	34.95	[34.26]	35.64	
ic Co	B203	10.43	10.73	10.61	9.65	10.14	9.92	10.08	9.93	
- ž	Al203	31.32	27.79	`31·18 <sup>´</sup>	31.27	30.87	31.11	30.00	29 41	
	Fe <sub>2</sub> O <sub>3</sub> .		·10				.50		2.90	
	FeO	1.14	•64	4.01	3.80	8.54	11.87	11.16	6.26	
	MnO						.09			
	Mg0	14.89	14.09	9.90	9.47	8.60	4.42	7.94	8.00	
	CaO	. 1.60	2.78	1.81	•98	1.33	•81	·65	1.65	
	Na <sub>2</sub> O	1.28	1.72	1.82	2.68	1.60	2.22	1.13	3.03	
. <del>.</del> .	) K <sub>2</sub> O	26	·16	·44	.21	.73	.24	.53	.16	
te	H20	3.32	3.83	3.77	3.79	3.44	3.62	3.63	2.94	
C S	) F							•55		
		100.00	100.42	100.00	99.87	100.00	100 35	100.23	101.32	
	( SiO.	38.85		39.01		37.50		27.99		
60-1	H.O.	9.31		9.89		1.91		1.64		
Or	(Ign	3:19		3.32		2.49		2.39		

	Alaba	isnka,		Brazil, Pierrepont, N. Y				
	Bla	ck.		Green.		Blac	k.	
1	Rm. 20.	J. & C. 57.	Rm. 32.	Rgs. 41.	J. & C. 64.	Rm. 35.	Rgs. 50.	
TiO2							•55	
( SiO <sub>2</sub>	35.44]	35.41	[35.90]	36 91	37.05	[34.98]	35.61	
$B_2O_3$	10.33	10.14	10.51	9.87	9.09	10.201	10.12	
Al <sub>2</sub> O <sub>3</sub>	30.41	33.75	37.81	38.13	40.03	27.18	25.29	
Fe <sub>2</sub> O <sub>3</sub>				•31			•44	
FeO	15.59	13.42	5.83	3.19	2.36	9.08	8.19	
MnO	·54		1.13	2.22	2.35			
MgO	1.88	1.22	·92	·04	.32	10.13	11.07	
CaO		.17		.38	.47	2.91	3.31	
Na <sub>2</sub> O	1.02	2.08	2.21	2.70	3.18	1.50	1.21	
K20	•47	.34	•42	·28			.20	
) Li <sub>2</sub> O			1.30	1.61	.60			
H <sub>2</sub> O	3.88	3.41	3.57	3.64	3.23	4.05	3.34	
) F	•76	·28	.70	•14	1.12		·27	
]	00.32	100.57	100.30	99.42	99.83	100.00	99.93	
(SiO2	36.19		38.06			36.64		
{ H <sub>2</sub> O	1.11		2.23			3.01		
( Ign	2.15		2.92			?		
	$ \begin{array}{c} TiO_2 \\ SiO_2 \\ SiO_2 \\ B_2O_3 \\ Fe_2O_3 \\ FeO \\ MgO \\ CaO \\ MgO \\ Na_2O \\ K_2O \\ H_2O \\ F \\ F \\ \end{array} $	$\begin{array}{c} A \ 1400 \\ Bla \\ Rm. 20. \\ TiO_3$	$\begin{array}{c c} Ald 0 \text{38}\text{nka}, \\ Black, \\ Rm. 20. J. & C. 57. \\ \hline \text{TiO}_{2} \\ \hline \text{SiO}_{2} \\ \hline \text{SiO}_{2}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

With the present interpretation of Rammelsberg's analyses the ratios of  $SiO_3$ :  $B_3O_3$  have been assumed as 4:1, while those of  $SiO_4$  to the total equivalent of hydrogen atoms in the different analyses are as follows:

No. 1	No. 7	No. 11	No. 12	No. 20	No. 32	No. 35
4:20.7	4:19.8	4:20.5	4:20.06	4:19.6	4:19.9	4:20.2

\*Compare the reference to this analysis on p. 115.

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The agreement between the corrected analyses of Rammelsberg and those of the other investigators is very remarkable, and the ratios of SiO<sub>2</sub> to the total equivalent of hydrogen atoms approximate closely to 4:20 (the average is  $4:20\cdot1$ ).

Seven complete analyses are also given by Rammelsberg and to them corrections for water have been applied, while the errors of the analysis have been distributed upon the SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. The results are given below, together with Rammelsberg's figures for SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O and loss on ignition :

No. o	f Analysis, 2	5	22	<b>24</b>	29	31	33
ď.	(SiO <sub>2</sub> [36.53]	[36.37]	[34.82]	[34.87]	[35.49]	[36.03]	[36.02]
or-	B2O3 [10.66]	[10.61]	10.16	[10.17]	10.35	10.51	10.51
Le C	Al <sub>2</sub> O <sub>3</sub> 32.90	33.12	35.46	<b>`</b> 33∙35	42.63	44.05	36.80
	FeO '66	2.88	13.12	11.95			6.38
	Mn0		.28	1.25	1.94	.92	.78
	MgO 11.79	10.89	1.52	.63	.39	.20	1.88
	CaO 1.25	•77			•45		
	Na <sub>2</sub> O 2·37	1.52	•98	1.75	2.60	2.00	2.47
	K <sub>2</sub> O •47		.09	•40	.68	1.30	•47
. v	) Li <sub>2</sub> O			·84	1.17	1.22	.72
or	$H_2O_{1} 3.00$	3.81	3.28	4.31	3.61	3.37	3.62
rec	) F ·64		•41	·82	1.18	.40	•55
	100.27	100.00	100.17	100.34	100.49	100.30	100.23
	(SiO2 38.09	38.33	36.11	36.22	38.19	38.85	38.46
· 50	B <sub>2</sub> O <sub>3</sub> 11.15	9.86	11.64	10.62	9.97	9.52	9.73
Da Da	$H_2O_{2.05}$	2.81	1.26	2.21	2.00	2.41	2.31
•	[ Ign 2.93	3.49	1.82	2.98	3.61	3.32	2.94

A comparison of the corrected analyses with the figures given by Rammelsberg indicate that  $B_2O_2$  has been determined with a good degree of accuracy. His water is always low and his silica high. The ratios of SiO<sub>2</sub> to the total equivalent of hydrogen atoms in the corrected analyses are as follows:

No. 2 No. 5 No. 22 No. 24 No. 29 No. 31 No. 33 Ratio 4:20.0 4:20.3 4:20.4 4:20.7 4:21.8 4:21.4 4:20.2

Two of the hydrogen ratios are very high; four of them approximate closely to 4:20.0; the average is 20.7.

<sup>4</sup>The results obtained by applying similar corrections to the remaining twenty analyses are given in the table on page 113, together with Rammelsberg's figures for SiO<sub>2</sub>, H<sub>2</sub>O and loss on ignition. In the last column the ratios of the total equivalent of hydrogen atoms are given, one quarter of the corrected SiO<sub>2</sub> being taken as unity.

The ratios of the silica to the hydrogen atoms in these twenty analyses exhibit a rather wide variation, from 4:18.7to 4:21.8. The average, however, is 4:20.4, and the average for all of his thirty-four analyses is also 4:20.4, or approximately 4:20.

	Ratio.	20.8	20.1	20.6	218	2.0-9	19.5	19.6	21.3	21.2	20.7	18-9	18.7	213	20.5	18-8	20.8	20.1	20.9	21.8	20-3	
1	Ign. ]	3.50	3.54	3.30	3.11	2.93	3.25	2.50	2.22	2.66	2.92	2 00	2.09	3.21	2.31	2.44	2.54	3-34	3.28	3-59	3-93	
ginal.	$H_2O$	2.82	3.04	2.80	2.61	2.43	2.75	2-29	1.72	2.11	2.48	1-45	1·74	2.34	1.54	1.81	1.90	2.00	2.60	2.49	2-57	
Ori	Si02	37.75	38.51	38-45	37.70	37-11	38-00	38-20	36-29	36.43	37.07	37.24	37.94	36-25	36-06	38.30	37-14	38.24	37-74	38-26	41.16	
	F	===================================	0.36 = 100.15	= 100.00	$\dots = 100.00$	=100.00	===================================	0.15 = 100.06	===================================	==100.00	0.31 = 100.13	=100.00	0.45 = 100.19	0.64 = 100.27	0.85 = 100.36	0.80 = 100.34	0.47 = 100.20	0.98 = 100.41	0.50 = 100.21	0.70 = 100.29	$1 \cdot 19 = 100 \cdot 50$	
Cor- rected	H <sub>2</sub> O	3 98	3-85	3.63	3.60	3-77	4.05	3.60	3.69	3.95	4.31	3.29	3.63	4.63	4.24	3 58	3-71	3.94	3.43	3-59	3-98	
	$Li_20$		, , , ,										-				0.32		0.74	0.48	0.41	
	$\mathbf{K}_20$	0.30	1370	0.73	0.43	0.32	0.28	0.25		0.30	0.30	0.82	0.65	0 46	0.58	0-33	0-75	0.38	0.34	0.21	2.17	
	$Na_20$	2.27	2.13	2-00	2.00	1.78	1.43	2.19	<b>†6</b> ∙1	1.36	2.04	1.93	1.39	1.43	1.36	2.37	2.30	2.04	2.40	1.53	1.37	
	CaO	0.88	0.16	0.71	1.25	0.80	1.31	0.72	1.02	0.44	1	0.62	0.50	0.40	0.72			0.30		0.62	8 1 1 1	
	MgO	11.62	10.46	9.11	9.51	9-43	7-27	77.9	6.32	3.84	3.49	3-65	2.62	2.3.2	0.78	1.06	1 68	4.30	0.41	1.62	19.0	
	0uM		0.36	60.0				0.58			16.0		0.40	1.50	0 11	2.68	1-87	3.59	2.51	1.53	96.0	
	FeO	4.36	2.80	2.98	4.42	89.1	7.23	9-93	13.23	11.58	12.55	11.64	13-82	12.82	17.40	10.30	10.52	5.43	1.38			
	$Al_{2}O_{3}$	30-86	32 55	34.56	34.26	31.26	31.41	30.02	30.44	34.12	31-86	31.63	30.22	32.21	30.34	31.53	34.15	33.19	41.89	43.97	41.83	
cted.	B203	[10.32]	[10.62]	[10.43]	[10-06]	[10.18]	[10.62]	[10.35]	[67.6]	[10.03]	[10.11]	[10.48]	[10.50]	[06.6]	[9.93]	[10.77]	[10.03]	[10.45]	[10.52]	[10.40]	[10.84]	
Corre	Si0 <sub>2</sub>	[35.41]	36.39]	[35.76]	[34.47]	34.88]	[36.40]	[35.48]	[33.57]	[34.38]	[34.65]	[35.94]	[36.01]	33.96	[34.05]	[36-92]	$[34 \cdot 40]$	[35.81]	[36.09]	[35.64]	[37.15]	
	Locality.	Eibenstock	Zillerthal	Texas, Pa.	Godhaab	Havredal	St. Gothard	Elba	Unity, N. H.	Krumman	DeKalb, N. Y.	Langenbeilau	Bovey Tracy	Krumbach	Andreasberg	Sarapulsk -	Elba	Elba	Elba	Shaitansk	Rozena	
	No.	ŝ	4	9	∞.	6	10	13	14	15	16	17	18	19	$2^{1}$	23	25	26	27	28	30	
Jour	R. S	CI	F	0U	RTI	I S	ER	IES	, V	OL.	V	Π,	N	0.	38.	]	Fei	BRU	AR	Y,	189	9.

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As already stated, Rammelsberg admits that his water determinations are too low; he also states that the formula for a complex mineral like tournaline cannot be determined from a few analyses but must be derived rather from the average of many determinations. If then it may be assumed that his loss on ignition, when corrected for the oxidation of the iron, gives a close approximation to the amount of water, his results on the whole agree with the formula  $H_{20}B_2Si_4O_{21}$ . It may also be stated that if the analyses are not corrected they lead to no satisfactory formula.

REVIEW OF RIGGS' ANALYSES.—Twenty analyses of American tourmalines were made by Riggs, and the ratios derived from them furnish the very best evidence of the accuracy of his results. The ratios are as follows:

					Total						Total
No.	SiO2	:	$B_2O_3$	:	hydrogen.	No.	$SiO_2$	:	$B_2O_3$	:	hydrogen.
36.	4	:	0.90	:	20.2	46.	4	:	0.96	:	20.2
37.	4	:	0.93	:	20.5	47.	4	:	0.98	:	20.08
38.	'4	:	0.95	:	19.5	48.	4	:	1.01	:	20.06
39.	4	:	0.94	:	19.7	49.	4	:	1.01	:	20.15
40.	4	:	0.96	:	19.3	50.	4	:	0.98	:	19.2
41.	4	:	0.95	:	19.7	51.	4	:	0.91	:	19.6
42.	4	:	0.92	:	19.8	52.	4	:	0.94	:	20.11
43.	4	:	0.94	:	20.03	53.	4	:	0.92	:	18.9
44.	4	:	0.88	:	20.2	54.	4	:	0.98		19.8
<b>4</b> 5.	4	:	0.92	:	20.03	55.	4	:	1.01	:	20.6

The average of these ratios is 4:0.95:19.88, or a very close approximation to 4:1:20, which indicates that tourmaline is derived from the acid  $H_{a_0}B_2Si_4O_{a_1}$ . It is pointed out by Riggs that "the boric acid found invariably falls short of the theory." This is generally, though not always, the case, and it is presumed that this slight defect in the analyses is due to the fact that it is not always possible to obtain a correct determination of boric oxide by the Gooch method without a second fusion of the silicate with sodium carbonate, which Riggs does not mention having made. It is not indicated by the ratios that these analyses "give as a general tourmaline formula the simple boro-orthosilicate R, BO, 2SiO," suggested by Riggs. The nearest approach to this is analysis No. 53, in which the ratio of SiO, to the total hydrogen is 4:18.9. The ratios with few exceptions show a very close approximation to the rational numbers 4:1:20. In eleven cases the numbers for the hydrogen ratios vary between the narrow limits 19.8 and 20.2. How exact the analyses must be in order to yield such ratios may be best understood when it is known that a difference of one-half of one per cent in the estimation of either silica or water would

change the numbers of the hydrogen ratio  $\pm 0.27$  in the one case and  $\pm 0.38$  in the other. If the silica were one-half of one per cent high and the water correspondingly low, the effect upon the ratio would be to change it from 4:1:20 to 4:0.99:19.35. The evidence is therefore convincing that, with the exception of analysis No. 53 (brown tourmaline from Gouverneur, N. Y.), the analyses of Riggs are very exact, and also that the material he analyzed was very pure.\* Referring to page 111, it will be observed that analysis No. 53 is the one which compares most unfavorably with Rammelsberg's corrected analyses. If the silica in this analysis were 1.25 per cent lower and the Al<sub>2</sub>O<sub>3</sub> correspondingly higher, the agreement with Rammelsberg's corrected analysis would be quite satisfactory, and the ratio would correspond with the theory. Leaving out of consideration this one analysis, which may be considered as either defective or made upon impure material, the average of the ratios of Riggs' analyses becomes 4:0.95:19.91.

The analyses of Riggs were very severely criticized by Rammelsberg, who characterized tourmaline analysis as "Kein Thema für Anfänger," but in the light of our present investigation we find the results very accurate, and it may justly be said that we are indebted to Riggs for the best series of tourmaline analyses that has ever been made. In fact, our conclusions regarding the composition of the mineral might readily have been deduced from his results alone.

REVIEW OF THE ANALYSES OF JANNASCH AND KALB.— Nine analyses were made, from which the following ratios have been calculated:

					Total						Total
No.	$SiO_2$	:	$B_2O_3$	:	hydrogen.	No.	$SiO_2$	:	$B_2O_3$	:	hydrogen.
56.	4	:	0.96	:	19.7	61.	4	:	0.95	:	<b>2</b> 0·2
57.	4	:	0.99	:	19.8	62.	4	:	0.80	:	20.00
58.	4	:	0.92	:	20.4	63.	4	:	0.98	:	19.7
59.	4	:	0.95	:	18.8	64.	4	:	0.84	:	20.01
60.	4	:	0.88	:	20.4	Average.	, 4	:	0.95	:	19.9

These analyses, like those of Riggs, bear every evidence of having been made with great precision, and the ratios, with the single exception of No. 59, approximate closely to 4:1:20, thus furnishing additional evidence that the acid from which all tourmalines are derived is  $H_{20}B_{2}Si_{4}O_{21}$ . The analyses do not

<sup>\*</sup>In a personal communication from Professor Riggs the following statement is made concerning the quality of the material investigated by him: "The material analyzed was of excellent quality, selected with great care. The colorless, pink and light green varieties were transparent, gem-like crystals, and the material of the rose-colored, brown and black varieties was, in my opinion, equally pure." Dated, Hartford, January 4th, 1899.

indicate the general formula R. BO, . 2SiO, proposed by Jannasch and Kalb. Their boric oxide determinations are in all cases a trifle too low for the theory, but it is believed that the reason for this is to be sought in imperfections of the method\* for determining this constituent in a complex silicate. The analyses are excellent, and they rank with those of Riggs, among the best analyses of tourmaline that have been made. From our own experience, however, it is very questionable whether tourmaline contains so much ferric iron as recorded in some of these analyses (2.90 to 6.68 per cent).

THE ANALYSES OF SCHARIZER .- The ratios of the three analyses are as follows:

No.	$SiO_2$	:	$B_2O_3$	: hydrogen.
65	4	:	0.20	: 20.9
66	4	:	0.76	: 21.0
67	4	:	0.74	: 20.2

By comparing these ratios with the ones which have been previously considered, it would seem that there are good grounds for believing that in these analyses the B<sub>2</sub>O<sub>3</sub> determinations are too low, and that the bases have not been determined with extreme accuracy. The ratios of SiO<sub>2</sub> to the total hydrogen atoms in the main substantiate the formula H<sub>20</sub>B<sub>2</sub>Si<sub>4</sub>O<sub>21</sub>.

ANALYSES FROM MISCELLANEOUS SOURCES.-In looking over the literature a number of analyses have been found which need to be recorded. They have been made partly for the purpose of identifying the mineral and partly for the purpose of determining the character of the tourmaline from special localities, but none of them have been made for the special purpose of determining the chemical composition of the species. It seems sufficient to give the ratios only, which are as follows:

					Total
	Locality.	Analyst.	${\rm SiO}_2$ :	$B_2O_3$	: hydrogen.
69.†	Mt. Bischoff	Sommerland	. 4 :	0.98	: 18.5
70.	Campolongo	Engelmann	4:	0.85	: 17.4
71.	Sysersk, Urals	Cossa and Arzrun	i4:	0.89	: 18.8
72.	Montgomery Co., Md.	Chatard	. 4 :	0.84	: 20.4
73.	Nevada Co., Cal	Melville	4:		: 20.8
74.	Tamaya, Chili	Schwarz	. 4 :	1.02	: 19.1
75.	Straschin, Bohemia	Weisner	. 4 :	1.10	: 19.4
76.	Urulza, Siberia	Stchusseff	. 4 :	0.82	: 19.0
77.	Kolar, India	Chapman Jones	. 4 :	0.87	: 19.1
		Average	. 4 :	0.95	: 19.2
		0			

\* Bodewig, Zeitschr. für Kryst., viii, p. 211, 1883. † 69, 70, 71 and 72 quoted in Dana's Mineralogy; 73, Bull. U. S. Geolog. Sur-vey, No. 90, p. 39; 74, Zeitschr. deutsch. Geol. Gesell., xxxix, p. 238; 75, Min. u. Petr. Mitth., ix, p. 410; 76, Zeitschr. Kryst., xx, p. 93; 77, Min. Mag., xi, p. 61.

As indicated by the variations in the ratios, the analysts apparently have not had sufficient experience to enable them to deal successfully with such a difficult problem as the tourmaline analysis. The average of the ratios, however, approximates to 4:1:20 and thus substantiates our formula.

TITANIUM IN TOURMALINE .- Titanium seems to have been overlooked in the earlier analyses of tourmaline, but is reported in several of the analyses of Riggs, Jannasch and Kalb, and others. The quantity, however, has always been found to be small, amounting to over one per cent (reckoned as TiO,) in only four of the analyses and to over 0.6 per cent in but two others. It has not been taken into consideration in making the foregoing calculations, partly because it would exert no appreciable influence on the final result, but chiefly because it is uncertain whether the titanium in this mineral plays the part of a tetravalent element replacing silicon, or of a trivalent element replacing aluminium. Although it may not be possible with the data now at hand to definitely settle this question, still the analyses furnish some evidence that the element should be regarded as trivalent. This result has been reached by considering titanium both as TiO, replacing SiO, and as Ti,O, replacing Al,O, and comparing the ratios derived from the four analyses in which the TiO, has been recorded as over one per cent. The results are as follows:

						Fotal
No.	Locality.	Premises.	$SiO_2$ :	$B_{2}O_{3}$ ]	hyo	drogen.
51.	Monroe, Conn., Riggs	$ \left\{ \begin{array}{l} {\rm TiO_2, 1.61 \ per \ cent} \\ {\rm Neglecting \ titanium} \\ {\rm Ti_2O_3 \ 1.45 \ per \ cent} \end{array} \right. $	n_4 n_4	0.88 0.91 0.91	:	$\begin{array}{c} 18 \cdot 9 \\ 19 \cdot 6 \\ 19 \cdot 97 \end{array}$
53.	Gouverneur, N. Y., Riggs	$ \left\{ \begin{array}{l} {\rm TiO_2 \ 1.19 \ per \ cent} \\ {\rm Neglecting \ titanium} \\ {\rm Ti_2O_3 \ 1.07 \ per \ cent} \end{array} \right. $	n_4	0·95 0·97 0·97	•••••	$18.5 \\ 18.9 \\ 19.2$
56.	Snarum, Jannasch and Kalb	$ \left\{ \begin{array}{l} {\rm TiO_2 \ 1\cdot 10 \ per \ cent} \\ {\rm Neglecting \ titanium} \\ {\rm Ti_2O_3 \ 0\cdot 99 \ per \ cent} \end{array} \right. $	n_4	0.93 0.96 0.96	••••••	19·1 19·7 19·9
59.	Tamatawe, Jannasch and Kalb	{ TiO <sub>2</sub> 1.22 per cent Neglecting titanium Ti <sub>2</sub> O <sub>2</sub> 1.10 per cent	n_4 n_4	0.90 0.92 0.92	••••••	18·4 18·8 19·1

In these four cases it will be observed that the calculations give the closest approximation to the normal tourmaline ratio when the titanium is regarded as  $Ti_2O_3$ . Moreover when the titanium is regarded as  $TiO_3$  the departure from the normal ratio is so great that it does not seem probable that this is due wholly to defects in the analyses. Some very careful and exact analytical work must be done in order to decide this question definitely.

CONSTITUTION OF TOURMALINE.—The evidence is convincing that all tourmalines are derivatives of a complex borosilicic acid H<sub>20</sub>B<sub>2</sub>Si<sub>4</sub>O<sub>21</sub>, and it is believed that further analyses will not alter this result, although they may furnish important data concerning the constitution of the acid. All of the hydrogen atoms of this acid in tourmaline are not replaced by metals, for the different varieties have always been found to contain water, which indicates the presence of hydroxyl. The ratio of the silica to the hydrogen derived from water (hydroxyl) plus the fluorine is not constant, but varies in Riggs' and our analyses from 4:3.14 (pale green tourmaline from Auburn, Maine) to 4:2.48 (colorless tourmaline from De Kalb). In all of the analyses in which water has been estimated directly, a sufficient quantity has been obtained to yield two hydroxyls in the formula; in only a few cases has the amount been sufficient to yield three hydroxyls. We are thus led to believe in the existence of two hydroxyls in all tourmalines, and it seems natural to associate them with the two boron atoms. The acid consequently becomes  $H_{1s}(B.OH)_{s}Si_{s}O_{1s}$ . The small amount of fluorine which is found in many varieties of tourmaline presumably plays the same role as hydroxyl, or is isomorphous with it, as in the case of topaz, of chondrodite, and of other minerals containing fluorine and hydroxyl. The slight excess of hydrogen over and above the two hydroxyls may be regarded as basic hydrogen, which plays the role of a metal. Such a relation is not unknown in complex mineral compounds.\*

One of the peculiar features of tourmaline is that varying proportions of metals of different valences and of essentially different character replace the hydrogens of the acid  $H_{19}(B.OH)_2Si_2O_{19}$ . In all cases thus far examined aluminium predominates and is present in sufficient quantity to replace more than half the hydrogens. From this it has been inferred that an aluminium-borosilicic acid  $H_{19}Al_{19}(B.OH)_2Si_4O_{19}$  is characteristic for all varieties of tournaline. The constitution of this acid may be expressed graphically as follows:



\* This Journal, xl, p. 396, 1890.

It would seem that the mass effect of the complex radical  $[Al_s(B.OH)_3Si_4O_{10}]$ , which has a valence of nine, is sufficiently pronounced to control or dominate all types of tourmaline. Thus it apparently makes no difference whether the nine hydrogens are replaced largely by aluminium and to a slight extent by alkalies; or largely by magnesium and to a slight extent by aluminium and alkalies; or to about an equal extent by aluminium, iron or magnesium and alkalies; the result in all cases is the mineral tourmaline, with its characteristic crystallization and its peculiar optical and electrical properties.

The following example (compare the ratio derived from the analysis of the green tourmaline from Haddam Neck, page 107) will illustrate the method of determining to what extent the nine hydrogens of the tourmaline acid, H, Al<sub>3</sub>(B.OH)<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>, are replaced by metals of different valences:

Ratio.	Total hydrogen			
equiva	lent, or 20 H.	2(OH, F). 18 H.	3 Al9 H,	
Al <sub>2</sub> O <sub>3</sub>	2.327	2.327	1.385 .942	$\div$ '154 = 6.1 R'''
FeO	•059 )			
MnO	.056 .160	.160	•160	154 - 118
MgO	.008	105	103	- 104 - 1110
CaO	·046 J			
$Na_{2}O$	.068 .178	.178	.178	$\div .154 - 1.2 \text{ R}'$
Li <sub>2</sub> O	.110 5 110	110	110	. 101 - 12 10
H <sub>2</sub> O	*344 + .404	·308 ·096	•0.96	$\div .154 = 0.6$ H
F,	.060 )			·
	20)3.078	2)2.770	9)1.385	9.0
	.154	1.385	.154	

From the ratio of the total hydrogen equivalent,  $\frac{2}{25}$  (representing two hydroxyls) are deducted. The remainder, 18 H, is divided by two, thus determining the ratio of the nine H's replaced by Al, in the formula. The excess of the aluminium or trivalent metal ratio, R''', together with the ratios of the bivalent metals, R', the alkali metals R' and the excess of hydrogen, H, represent nine H's, which are divided among the different constituents. Thus in the green tournaline from Haddam Neck 6.1 hydrogens are replaced by Al (R'''), 1.1 by R'', 1.2 by R' and there remains 0.6 excess of basic hydrogen.

The analyses of Riggs, Jannasch and Kalb, Scharizer and Chatard, given on page 555 of Dana's Mineralogy, together with our own analyses, practically include all varieties of tourmaline which have thus far been investigated, and in the following table are given the results of applying the foregoing method of calculation to them :

# 120 Penfield and Foote-Composition of Tourmaline.

		No.	Locality.	Color.	Analyst.	R'''	R''	R'	н
	ſ	1	Minas Geraes, Brazil	Pale-pink _	Riggs, 37	6.7	0.3	1.2	0.8
		2	Rumford, Me.	Rose	Riggs, 36	6.2	0.5	1.2	1.1
SS.		3	Brazil	Green	Jann. & Kalb, 64	6.3	1.1	0.9	0.7
ň		4	Auburn, Me.	Colorless	Riggs, 38	6.5	0.6	1.1	1.1
al		5	Minas Geraes, Brazil	Pale-green	Riggs, 39	$6 \cdot 2$	0.8	1.3	0.2
8		6	Schüttenhofen, Bohemia_	Red	Scharizer, 67	6.1	0.3	1.3	1.3
no -	{	7	Haddam Neck, Conn.	Pale-green_	Authors	6.1	1.1	1.2	0.6
Ē		8	Barra do Perahy, Brazil	Green	Jann. & Kalb, 63	6.0	1.1	1.4	0.2
lia		9	Rumford, Me.	Dark-green	Riggs, 42	6.0	1.3	1.1	0.6
ith		10	Minas Geraes, Brazil	Olive-green	Riggs, 41	5.9	1.1	1.3	0.2
Ţ		11	Auburn, Me	Light-green	Riggs, 40	5.7	0.9	$1 \cdot 2$	1.5
		12	Schüttenhofen, Bohemia_	Blue-green	Scharizer, 66	5.2	1.5	1.2	1.1
	U	13	Auburn, Me	Dark-green	Riggs, 43	5.3	1.2	1.1	1.1
- · ·	$\left( \right)$	14	Buckworth, Australia	Black	Jann. & Kalb, 62	4.7	2.9	0.7	0.2
ed		15	Paris, Me	Black	Riggs, 44	4.7	3.0	0.2	0.8
pt		16	Auburn, Me	Black	Riggs, 45	4.7	3.1	0.2	0.2
E B3		17	Alabashka, Russia	Black	Jann & Kalb, 57	4.7	3.5	0.2	0.0
un s	{	18	Mursinka, Russia	Black	Jann. & Kalb, 60	4.7	3.5	0.7	0.4
21		19	Schüttenhofen, Bohemia_	Blue-black_	Scharizer. 65	4.2	3.0	0.2	1.0
E d		20	Piedra Blanca	Black	Jann. & Kalb, 58	4.4	3.2	0.6	0.8
2N		21	Montgomery Co, Md	Green $(Cr)$	Chatard, 72	4.4	3.4	0.2	0.2
H	l	22	Minas Geraes, Brazil	Black	Riggs, 46	4.3	3.2	0.2	0.7
	ſ	23	Stony Point, N. C	Black	Riggs, 48	$4 \cdot 2$	3.6	0.2	0.2
s.		24	Oláhpian	Black	Jann. & Kalb, 61	40	4.1	0.5	0.4
ne	1	25	Tamatawe	Black	Jann. & Kalb. 59	3.8	46	0.5	0.1
ali.	;	26	Haddam, Conn	Black	Riggs, 47	3.7	4.0	0.5	0.8
m		27	Snarum, Norway	Black	Jann. & Kaib. 56	3.7	4.4	0.7	0.2
an an a	i	28	Orford, N. H.	Dark-br'wn	Riggs, 52	3.6	4.1	0.6	07
Ha		29	Monroe, Conn.	Dark-br'wn	Riggs, 51	3.4	4.1	0.7	0.8
~	i I	30	Nantic Gulf, Baffin's Ld.	Black	Riggs, 49	3.1	47	0.5	0.7
ia I	2	31	DeKalb, N. Y.	Colorless	Authors	2.5	57	0.3	05
ma		32	DeKalb, N. Y.	Colorless	Riggs, 54	2.2	57	0.4	0.7
181		33	Gouverneur. N Y	Brown	Riggs, 53	2.2	5.6	0.4	0.8
Iou		34	Hamburg, N. J.	Brown	Riggs, 55	2.0	6.2	0.2	0.6
Mg &		35	Pierrepont, N. Y.	Black	Riggs, 50	1.6	63	0.4	0.7
re. (	1							.1	

It will be observed that the extent to which the nine hydrogens of the acid  $H_{\bullet}Al_{2}(B.OH)_{*}Si_{*}O_{19}$  are replaced by metals, is very variable. The trivalent metal, R''', is chiefly aluminium, and the extent to which the hydrogens are replaced by it ranges from 6.7 to 1.6. The bivalent metals represented by R'' are chiefly iron and magnesium, and the extent to which the hydrogens are replaced by them ranges from 0.2 to 6.3. In general R'' and R''' are reciprocal. There is always some hydrogen replaced by the alkali metals R', and some basic hydrogen. The results are arranged in the table according to a decrease in the replacement of the hydrogens by R'', and according to this arrangement the different varieties of tourmaline fall into natural groups.

The first 13 examples are characterized by containing an appreciable quantity of lithium, while in the others none, or

not more than traces of this element have been found; these may therefore be designated as *Lithia Tournalines*, which form a natural group. In this group R' is higher than in other varieties, while H is somewhat higher than the general average; R''' is very high and R'' correspondingly low. This variety of tournaline has its particular mode of occurrence, being found in pegmatite veins associated with quartz, albite, microcline, orthoclase, muscovite and lepidolite. The material is generally delicately colored and often transparent and of gem-like quality. It is difficultly fusible when heated before the blowpipe, fusibility= $5-5\frac{1}{2}$ .

At the opposite extreme, 31-34, are varieties which may be designated as Magnesia Tourmalines. In these R", which is chiefly magnesium, is very high and R'' correspondingly low, while R' reaches its lowest limit, 0.2 to 0.4. These varieties are light-colored and at times of gem-like quality. They are easily fusible before the blowpipe, fusibility = 3. With these No. 35 should be associated, for it differs only in containing considerable iron which is isomorphous with the magnesium, hence the color of this tourmaline is black. The last five are alike in their mode of occurrence. They have probably been formed in limestones containing magnesium by the contact action of intruded igneous masses during the pneumatolitic period, when such masses were giving off heated aqueous vapors containing boracic acid and fluorine compounds. They are found in coarse crystalline limestone, associated with graphite, phlogopite, pyroxene, amphibole, scapolite and apatite. Contact metamorphisms of this nature have recently been described by Lacroix.\*

The intermediate varieties (Nos. 14 to 30) with the exception of No. 21 are black or dark brown, owing to the presence of iron. These are the ordinary tourmalines found in granites, gneisses and schists, and sometimes in pegmatite veins intimately associated with lithia tourmaline, as at Auburn and Paris, Maine. They too have probably resulted from the mineralizing action of heated aqueous vapors containing boracic acid and fluorine compounds, given off during the pneumatolitic period of cooling igneous rocks. A contact metamorphism of this character, attended by the formation of tourmaline vein stone, has been very carefully described by Hawes.<sup>†</sup>

Nos. 14 to 22 (No. 21 excepted) are characterized by containing iron and only a little magnesia, hence they may be designated as *Iron Tourmalines*; Nos. 23 to 30 contain both

<sup>\*</sup> Le Granites des Pyrénées et ses Phenomènes de Contact, Bull. Carte Géologique de France, No. 64, Tome x, p. 54, 1898.

The Albany Granite, New Hampshire, and its Contact Phenomena, this Journal, xxi, p 21, 1881.

magnesia and iron, and are hence designated as *Magnesia-Iron Tourmalines*. These two groups, however, grade into one another. The fusibility of these intermediate groups of tourmalines varies from 4.5 to 3, and decreases as the amount of iron and magnesia increase.

Although in this series of thirty-five analyses there are pronounced groups or types of tourmaline which may be recognized, nowhere in the series do the ratios of  $\mathbb{R}''$ ,  $\mathbb{R}''$ ,  $\mathbb{R}'$  and H approximate so closely to rational numbers that a definite formula for any one type can be instituted. Riggs and Jannish and Kalb, however, have given special formulas for different types of tourmaline (pages 100 and 101) based upon multiples of the acid  $\mathrm{H}_{i0}(\mathrm{B.OH})_{3}\mathrm{Si}_{4}\mathrm{O}_{i9}$ . Deducting from their formulas appropriate multiples of the aluminium-borosilicic radical  $[\mathrm{Al}_{3}(\mathrm{B.OH})_{2}\mathrm{Si}_{4}\mathrm{O}_{i9}]$ , it is found that the nine variable hydrogens of the tourmaline acid are replaced by metals of different valences in the following proportions:

		R'''	$R^{\prime\prime}$	R'	H
I.	Lithia tourmaline {	Riggs	0.0	1.3	0.7
		Jann. and Kalb 6.0	1•4	1.3	0.3
II.	Iron tourmaline $\left\{ \begin{array}{c} 1 \\ 1 \\ \end{array} \right\}$	Riggs	2.6	0.7	0.7
		Jann. and Kalb5.0	3.0	0.5	0.3
III.	Iron-magnesia tour.	Jann. and Kalb4.0	4.0	0.2	0.3

Concerning the formulas for lithia tourmaline, Riggs' corresponds closely to No. 1, and Jannasch and Kalb's to Nos. 7, 8, 9 and 10 of our series (compare the table on p. 120), but neither of these complicated formulas furnishes a satisfactory expression for this type as a whole. Similar statements might be made concerning their formulas for iron tourmalines and for iron magnesia tourmalines. The endeavor to express the composition of tourmaline or of one of its types by a definite formula may be compared to the attempt to express the composition of the dark varieties of sphalerite by a formula. Thus Zn, Fe<sub>4</sub>S<sub>15</sub> would correspond to sphalerite, containing about 50.5 per cent of zinc and 15.7 per cent of iron, but zinc and iron are isomorphous and can mutually replace one another in sphalerite, and a variety containing less iron would have to be expressed by a different formula. When, however, we understand the isomorphous relations existing between zinc and iron, and express the composition by RS, where R=Zn and Fe, the composition becomes very much simplified.

In tourmaline we have an isomorphous relation of a very peculiar nature, for in the acid H<sub>2</sub>Al<sub>3</sub>(B.OH)<sub>2</sub>Si<sub>4</sub>O<sub>19</sub> the nine hydrogens may be replaced to a large extent either by the trivalent metal aluminium or by the bivalent metals magnesium
and iron without any decided change in crystalline form. This leads to the consideration of a certain phase of isomorphism which, as it seems to us, has not been considered with sufficient care, namely, the mass effect of complex radicals in influencing or controlling crystallization. Thus in their simple salts we do not regard sodium and potassium as isomorphous with calcium, but in some complex silicates, zeolites for example, we recognize Na<sub>2</sub> and K<sub>2</sub> as isomorphous with, or at least capable of replacing, calcium, barium and strontium. In some of the phosphates, dickinsonite and fillowite for example, we have sodium (Na<sub>2</sub>) playing the same role as calcium, manganese and iron in replacing the hydrogens of phosphoric acid. In the garnet-sodalite group we have minerals with isometric crystallization, to which the following formulas have been assigned:\*

 $\begin{array}{c} Ca_{s}Al_{2}(\mathrm{SiO}_{4})_{s} \ \mathrm{Grossularite} \\ Fe_{s}Al_{3}(\mathrm{SiO}_{4})_{s} \ \mathrm{Almandite} \\ (Cl-Al)Na_{4}Al_{2}(\mathrm{SiO}_{4})_{s} \ \mathrm{Sodalite} \\ (NaSO_{4}-Al)Na_{4}Al_{2}(\mathrm{SiO}_{4})_{s} \ \mathrm{Noselite} \\ (NaSO_{4}-Al)(Na_{2}, Ca)_{2}Al_{2}(\mathrm{SiO}_{4})_{s} \ \mathrm{Ha\"uynite} \\ (NaSO_{4}-Al)(Na_{2}, Ca)_{2}Al_{3}(\mathrm{SiO}_{4})_{s} \ \mathrm{Lazurite} \\ (Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)(Output)$ 

When it is taken into consideration that isometric crystallization is exceptional in the group of silicates, we are led to believe that the sexivalent radical [Al<sub>2</sub>(SiO<sub>4</sub>)<sub>5</sub>], by virtue of its mass effect, controls or dominates the crystallization of these minerals. Not only are they isometric, but, with the exception of zunyite, which is tetrahedral, they all crystallize commonly in dodecahedrons. In sodalite, noselite and lazurite, such unlike constituents as chlorine, and the univalent sulphate and polysulphide radicals (NaSO<sub>4</sub>)' and (NaS<sub>3</sub>)' play the same part in the complex molecules. It is moreover probable that these unlike constituents are isomorphous in the sense that they can mutually replace one another, for Brögger and Bäckström have described homogeneous material containing the lazurite, haüynite and sodalite molecules, while appreciable quantities of chlorine are almost always found in noselite and haüynite, thus indicating the presence of the isomorphous sodalite molecule. It is to be expected that the larger and more complex the radical the more potent will be its mass effect in controlling or determining the crystal form. Thus in sodalite, noselite and haüynite the radical is very large,  $[R'_{A}Al_{2}(SiO_{A})_{3}], R'_{A}=Na_{A} \text{ or } Ca_{2}.$ 

Tourmaline, it would seem, furnishes an example somewhat analogous to that presented by the garnet-sodalite group. In

\* Brögger and Bäckström, Zeitschr. für Kryst., xviii, p. 209, 1890.

this acid H<sub>2</sub>Al<sub>2</sub>(B.OH)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>, the mass effect of the complex radical [Al<sub>4</sub>(B.OH)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>] is so great, or, the role played by the replacement of the nine hydrogens is so subordinate, that the bivalent elements, Fe, Mg, Mn and Ca, and to a slight extent the alkalies, Li, Na and K, can replace aluminium as isomorphous constituents. This conclusion in some respects is analogous to that reached by Rammelsberg, who stated in 1870 that all tourmalines were derived from an acid H<sub>2</sub>SiO<sub>6</sub>, in which the six hydrogens were replaced in varying proportions by R'<sub>6</sub>, R''<sub>4</sub>, Al<sub>4</sub> and B<sub>2</sub>. Applying Rammelsberg's idea to the acid H<sub>18</sub>(B.OH)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>, all varieties of tourmalines may be regarded as mixtures of the molecules

 $R'_{15}(B.OH)_{2}Si_{4}O_{16}, R' = Li, Na, K and H$  $R''_{9}(B.OH)_{2}Si_{4}O_{16}, R'' = Fe, Mg, Mn and Ca$  $R'''_{6}(B.OH)_{2}Si_{4}O_{16}, R''' = Al, Cr and small amounts of Fe and Ti.$ 

It seems more logical and satisfactory, however, to consider all varieties of tourmalines as salts of the acid  $H_{\bullet}Al_{\bullet}(B.OH)_{s}$  $Si_{\bullet}O_{s}$ , in which the complex aluminium-borosilicic acid radical  $[Al_{\bullet}(B.OH)_{s}Si_{\bullet}O_{s}]$  exerts a mass effect by virtue of which the remaining hydrogens may be replaced by metals of essentially different character without bringing about any pronounced change in crystalline form.

# Note concerning the detection of ferrous and ferric iron in Silicates ; by S. L. Penfield and H. W. Foote,

In the preliminary work connected with the study of the methods of the tourmaline analysis, considerable time was devoted to ferrous and ferric iron determinations. The ordinary method of dissolving in a mixture of hydrofluoric and sulphuric acids and titrating with potassium permanganate can not be applied readily to tourmaline because it is extremely difficult to dissolve the mineral. Riggs overcame this difficulty by using very fine powder and heating under pressure in a heavy platinum crucible provided with a lid which was held down by clamps. Jannasch and Kalb succeeded in decomposing the exceedingly fine, elutriated powder by heating in sealed glass tubes with a mixture of sulphuric and hydrofluoric acids, but the method was far from satisfactory. We have employed fusion with borax. In order to test the method, silicates containing varying proportions of ferrous and ferric iron were first carefully standardized by the method described by Pratt.\* The powdered silicate and borax glass were then fused in a platinum boat in a combustion tube, through which a current of either nitrogen or carbon dioxide gas was conducted. These

\* This Journal, xlviii, p. 149, 1894.

gases were first freed from all traces of oxygen by conducting them over a roll of heated bright copper gauze at one end of the tube. Decomposition is thus readily effected without any appreciable oxidation. After fusion the material can be dissolved in dilute sulphuric acid and titrated with potassium permanganate. With small quantities of iron the method gives very satisfactory results, but ferric iron suffers a slight reduction during fusion, hence the method can not be recommended as a quantitative one when accuracy is required. The amount of reduction is nearly proportional to the amount of ferric iron, and when about 6 per cent of Fe<sub>2</sub>O<sub>3</sub> is present the error amounted to about 0.3 per cent. It is certain, however, that very satisfactory determinations of ferrous and ferric iron might be obtained by means of this method, by applying a correction which could be determined by experimenting with some artificial mixture of silicates containing approximately the same amount of ferric oxide as the mineral. It is difficult to understand the cause of this reduction, which was first noted by Rammelsberg,\* and afterwards carefully studied by Suida.† Fusion with borax furnishes, however, a most excellent

means for decomposing insoluble silicates, when qualitative tests for ferrous and ferric iron are desired. The application of the method is as follows: The mineral and some borax glass are heated in a closed-tube over a Bunsen-burner flame until decomposition is complete, or nearly so. Water is then dropped upon the hot glass in order to crack it, and, when cold, the end of the tube is broken up and transferred to a test-tube. About 3<sup>cc</sup> of dilute hydrochloric acid are then added, and the acid is boiled vigorously until the material is dissolved, when about 5<sup>cc</sup> of cold water are added. The liquid, after being divided into two portions, may then be tested with potassium ferricyanide for ferrous iron, and with either ammonium thiocyanate or potassium ferrocyanide for ferric iron. The results are very satisfactory and decisive, and although there is a tendency for ferric iron to undergo slight reduction during fusion, and also a tendency for ferrous iron to undergo slight oxidation during the manipulation, these defects are so triffing that practically they may be disregarded.

Mineralogical-Petrographical Laboratory,

Sheffield Scientific School, January, 1899.

\* Zeitschr. der deutsch. geolog. Gesell., xxiv, p. 69, 1872.

1 Min. Mittheilung, Tschermak, 1876, p. 175.

## 126 H. A. Pilsbry—Littoral Mollusks from Patagonia.

## ART. XIII.—Littoral Mollusks from Cape Fairweather, Patagonia; by HENRY A. PILSBRY. (With Plate I.)

In the course of his paleontological explorations in Patagonia in the interest of Princeton University, Mr. J. B. Hatcher found time to make a small gathering of marine shells, at the locality named above. The scarcity of information upon the fauna of the east coast of South America makes it desirable to place the facts gained from even small collections on record, to the end that the limits of the faunal provinces of this coast may be more exactly defined, and their characteristics more fully exposed.

The fauna at the point in question is typically Magellanic, with but little admixture of types from the Argentine fauna of La Plata region. Nacella, Photinula and Trophon, Plaaiphora and littoral Brachiopoda, all occurring in a gathering so small as this, at once indicate the western and not northern origin of this mollusk population. Bullia alone is more northern in distribution, this being its most southern outpost.

The addition of the genus *Sphenia* to the Magellanic fauna is interesting and unexpected.

The figures on Plate I are three-fourths natural size.

### MURICIDÆ.

Trophon Gerversianus Pallus. Trophon Gerversianus Phillipianus Dkr. Trophon fasciculatus Hombron and Jacquinot. Trophon textiliosus Hombr. and Jacq. Pl. I, fig. 4.

Shell fusiform, white or slightly buff tinted, with moderately dilated body-whorl and short oblique or subvertical anterior channel. Whorls about 6, convex, separated by a deep suture, the last dilated toward the lip. Sculpture of numerous subregular rounded spiral cords (28-34 on body-whorl, 8-11 on penultimate whorl), separated by much narrower linear grooves, and numerous vertical folds, which are rather closely placed, separated by intervals narrower than themselves, are somewhat arcuate in harmony with the lines of growth and become obsolete upon the base. There are about 20 (18-21) folds upon the penultimate whorl, pretty regular and equal; but upon the latter part of the last whorl they become irregular or in part obsolete. Aperture ample, over half the total length of the shell, the outer lip somewhat expanding and faintly crenulated; columellar lip with a smooth white callous, reflexed over and closing the axial chink; siphonal fasciole well developed.

> Alt. 36, diam. 23 mm.; alt. of aperture 22 mm. " 39 " 21 " " " " 21 "

The original description and figures were from a young shell. The species has not hitherto been recognized, probably owing to this circumstance. Mature specimens collected by Mr. Hatcher are here described and illustrated. The figures referred to *decolor* Phil. in the Voyage au Pol Sud. (Zool., pl. 25, f. 6-8), look like adults of *textiliosus*.

T. textiliosus has been reckoned a synonym of T. Gerversianus by Tryon (Man. Conch. II and III), but this is only another example of the "lumping" practised by him in dealing with Trophon.

It differs conspicuously from most other Cape Horn Trophons in its less rude sculpture and symmetrical contours. *T. decolor* Phil. has a much shorter anterior canal, purple interior and fewer spirals. In *T. cancellinus* Ph. the lip is thickened and dentate within. *T. crispus* Gld. differs in sculpture; and *T. liratus* Couth., which is apparently the most nearly allied species, has the anterior canal longer, and there are fewer spiral grooves. Specimens are in the collection of the Academy of Natural Sciences of Philadelphia from "Santa Cruz River, Patagonia, Wm. Bell."

#### BUCCINIDÆ.

Euthria plumbea Phil.

*Enthria* sp. undet. Like *plumbea*, but finely spirally striated throughout. All of the specimens are beach-worn and not suitable for description.

Bullia globulosa Kiener.

VOLUTIDÆ.

Scaphella Ferussaci Don. Scaphella ancilla Sol.

## CALYPÆTRIDÆ.

Trochita corrugata Reeve. Varies toward forms in which the radial ribs almost disappear.

#### TROCHIDÆ.

Photinula cœrulescens King. Photinula tœniata Wood.

*Photinula pruinosa* Mab. and Roch. Quite distinct from the longer-known species in its Gibbula-like contour and wide, flattened, lusterless columella.

## PATELLIDÆ.

Nacella ænea magellanica Gmel. Nacella ænea deaurata Gmel.

MOPALIIDÆ.

Plaxiphora setigera King.

### PECTENIDÆ.

Pecten patagonicus King.

#### Myidæ.

# Sphenia Hatcheri n. sp. Pl. I, figs. 5, 6.

Shell cretaceous and dull, stout, rather strong, moderately inflated, with broad, somewhat truncated, closed anterior, and narrow, abruptly truncate and widely gaping posterior end. Beaks small, in close contact and eroded at the tips, nearly median, being one mm. nearer the posterior than the anterior end; projecting somewhat above. Dorsal margin highest anterior to the beaks, thence sloping downward and posteriorly; anterior end widely subtruncate, arcuate; ventral margin slightly arcuate. Sculpture, fine, nearly regular concentric grooves separating wider intervals on the anterior portion of shell, disappearing posteriorly, where there are only some rude, irregular wrinkles at unequal intervals. Face of the chondrophore in right valve directed ventrally; that of the left valve partially erect. Interior white or stained, porcellanous, the adductor scars distinct, pallial line and very broad posterior sinus indistinct. Length 17, altitude 9.5, diam. 7.2mm. A single specimen collected. The genus has not before been reported from this region to my knowledge.

### MACTRIDÆ.

Mactra (Mactra s. str.) Jousseaumi Mabille and Rochebrune. Pl. I, figs. 1, 2, 3.

The specimen figured, one of several collected, agrees with Mabille and Rochebrune's short and unsatisfactory description<sup>\*</sup> as far as that goes, except in size; their specimen measuring, length 45, alt. 34, diam.  $18^{mm}$ . The proportions however are similar, the figured specimen measuring 67, 48,  $28^{mm}$ . The subtriangular form, perfectly straight slope of the valve margins in front of the beaks, and obtuse siphonal extremity, as well as the details of hinge structure, are sufficiently shown in the figure. In external texture it is like an old *Spisula solidissima*, but the thin, light yellowish-olive cuticle adheres in small ragged patches.

### MYTILIDÆ.

Mytilus magellanicus Gmel. Mytilus sp. A single small specimen. Mytilus edulis L.

### TEREBRATELLIDÆ.

Terebratella dorsata Gmel.

Academy of Natural Sciences, Philadelphia.

\* Miss. Sci. du Cap Horn, Mollusques, p. 106.

# ART. XIV .- The Thermodynamic Relations for Steam; by G. P. STARKWEATHER.

AMONG the various thermodynamic relations for a gas that between pressure, volume and temperature, the 'equation of condition' is one of the most important. To apply to the case of steam such equations, either empirical, or based on assumptions hardly justifiable, have been formed by Zeuner,\* Schmidt,+ Ritter,‡ and Antoine.§ Of these Zeuner's and Schmidt's satisfied the saturation line well, but they, as well as Antoine's, had the fatal defect that the constant which determines the limiting value of  $\frac{pv}{rr}$  for very great volumes was assumed incorrectly.

Van der Waals' celebrated pamphlet in 1873 gave a rational form to the equation of condition, and Clausius' generalization of the same,

$$p = \frac{\mathrm{RT}}{v-a} - \frac{f(\mathrm{T})}{(v+\beta)^2},$$

has been for the most part adopted for various substances. Equations based upon this generally have the aim of satisfying not only the gaseous state but also the liquid. A relation between  $\alpha$  and  $\beta$ , and also the value of  $f(\mathbf{T})$  at the critical point, follow from the fact that at that point not only does this equation hold, but also its first and second partial derivatives with respect to v. R is fixed by the chemical composition of the substance, while f(T) is so determined as to satisfy the corresponding saturation pressures and temperatures by Clausius' method. The value of  $\alpha$  (hence  $\beta$ , from the relation mentioned above) is so chosen as to satisfy the water line at some point.

The best application of this method to steam has been given by Van Laar, \*\* who has taken for f(T) the form adopted by Sarrau<sup>++</sup> for carbonic acid,  $\kappa \gamma^{-T}$ ,  $\kappa$  and  $\gamma$  being constants. On applying Clausius' method of determining the corresponding saturation pressures and temperatures to the equation he has found a good agreement.

\*Zeitschr. des Ver. Deutsch. Ingen., xi, p. 42, 1867.

Zeitschr. des Ver. Deutsch. Ingen., xi, pp. 649, 771, 1867, and Prag Abhandl., i, 1868.

Wied. Ann., iii, p. 447, 1878.
Comptes Rendus, ex, p. 632, 1890.
Wied. Ann., xiv, pp. 279, 692, 1881.
Wied. Ann., xiv, p. 692, 1881.
\*\*Zeitschr. für Phys. Chem., xi, p. 433, 1893.
Comptes Rendus, ci, pp. 941, 994, 1145, 1885.

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But Van Laar's equation does not satisfy the saturation volumes. The writer has shown in a previous paper\* that the saturation volumes as calculated from Regnault's latent heats are entirely out of accord with those directly measured by Battelli,† and has given reasons for preferring the former. From these Van Laar's equation deviates 2.5 per cent. Even should we assume Battelli's experiments to be correct instead of Regnault's the deviations would still exceed 1 per cent.

Were it certain that the equation were necessarily of Clausius' form, holding for the liquid as well as the vapor, the method would be exact, and we should simply have to say so much the worse for the experiments. But all we know concerning the last term of the second member is that at large volumes at any given temperature it must be sensibly  $\frac{c}{v^*}$ , as has been shown by Van der Waals. If we replace  $\frac{1}{(v+\beta)^2}$  by some other function of v which is sensibly  $\frac{1}{v^2}$  at large volumes, the application of Clausius' method becomes very complicated, if not, indeed, impossible. The failure of Van Laar's equation to satisfy the facts would seem to show that the form  $\frac{f'(T)}{(v+\beta)^a}$  is not sufficiently correct for the water line, at least.

Abandoning the attempt to satisfy the water line throughout, we might still consider  $\frac{f(\mathbf{T})}{(v+\beta)^2}$  as sufficiently accurate for it in the vincinity of the critical point, the relations for that point still holding true. The equation would thus apply to steam for all states. In this case, if we give the equation Clausias' general form, his method for determining  $f(\mathbf{T})$  does not apply, and we are free to choose it so as to satisfy the saturation volumes. This has apparently never been done. The writer has attempted it, but without success.  $f(\mathbf{T})$  would necessarily decrease very rapidly with increasing temperature. Thus at 100° C., 200° C. and 365° C. (the critical temparature)  $f(\mathbf{T})$ would have the respective values 59.5, 21.5 and 13.5. Moreover, the great fall from 100° to 200° is out of accord with the change from 200° to 365°. This seems to indicate that the type of formula selected will not satisfy the facts.

There remains the following problem, to obtain equations which shall satisfy the experiments within ordinary limits. Such equations would suffice for most purposes, and moreover the writer hopes to draw from them some theoretical conclu-

<sup>\*</sup> This Journal, Jan. 1899, p. 13.

<sup>+</sup> Mem. R. Acc. Sc. di Torino (ii), 43, 1893.

sions of interest. A p-v-T equation should be of the form

 $p = \frac{\mathrm{RT}}{v - a} - f(\mathrm{T}) \phi(v) \,.$ 

In this R must have its theoretical value deduced from the chemical composition of water, while a, on account of the extreme incompressibility of water, should have a value not much less than 0.001, v being in cubic meters per kilogram. Moreover,  $\phi(v)$  must be sensibly  $\frac{c}{v^2}$  for large values of v.

The writer has formed the following equation, to hold for volumes not much less than 0.12 cubic meters per kilogram. At such volumes it should not be used when the pressure much exceeds 11700<sup>mm</sup>, although for larger volumes it may be applied to higher pressures.

$$p = \frac{\mathrm{RT}}{v-a} - \frac{\mathrm{A}}{\mathrm{T}v^{\frac{3}{2}}(v^{\frac{1}{2}} + \gamma)}$$

If p is expressed in millimeters and v in cubic meters per kilogram the constants are

log	$\mathbf{R} =$	0.539990	α =		0.0008
log	A =	4.632127	γ =	=	1.20484

The value of R is that given by Van Laar,\* modified by the fact that he places the absolute zero at  $-273^{\circ}2$  instead of  $-273^{\circ}7$ , as assumed here.

How well the equation agrees with the saturation line is shown by the following table. In the first column is given the temperature absolute, in the second the pressure,  $p_c$ , calculated from the formula by means of the saturation volumes, in the third the pressure according to Regnault,  $p_{\rm R}$ , and in the fourth the fractional deviation, d, of  $p_c$  from  $p_{\rm R}$ .

т	$p_{ m C}$	$p_{ m R}$	d	т	$p_{ m C}$	$p^{\mathrm{R}}$	d
313.7	55.11	54.91	+.0036	403.7	2026.4	2030.3	0019
323.7	92.37	91.98	+.0042	413.7	2712.2	2717.6	0020
333.7	149.34	148.79	+.0037	423.7	3573-3	3581.2	0022
343.7	233.66	233.08	+.0025	433.7	4641.7	4651.6	0021
353.7	355.04	354.62	+.0012	443.7	5950.9	5961.7	0018
363.7	525.64	525.39	+.0005	453.7	7538.1	7546.4	0011
373.7	760.01	760.00	- 0	463.7	9442.7	9442.7	0
383.7	1074.6	1075.4	0008	473.7	11700	11689	+.0008
393.7	1489.5	1491.3	0012				

With the exception of those near  $323^{\circ}$ .7 the variations are insignificant, but the change in sign at  $463^{\circ}$ .7 shows that the

\* Zeitschr. für Phys. Chem., xi, p. 433, 1893.

equation will not hold for much smaller volumes. The larger deviations near  $323^{\circ.7}$  are not due to the form chosen for the equation, for at such large volumes the gas deviates only slightly from the law of Boyle and Charles. A sufficient explanation for these deviations lies in the values of p and  $\frac{dp}{dt}$ , Regnault's formula for which is incorrect at low pressures, due to the fact that he did not recognize the sudden change in  $\frac{dp}{dt}$  at 0°. This matter will be considered later.

p and T being given, the formula is not convenient for obtaining v, but if an approximate value of v be found from Boyle and Charles' law, p obtained, and then v corrected by the assumption

$$\delta \log p = -\delta \log v,$$

a second correction will generally be sufficient.

If the factor  $\frac{1}{T}$  is correct, the term  $v^{\frac{3}{2}}(v^{\frac{1}{2}}+\gamma)$  must be sensibly so, for it satisfies the volumes on the saturation line and approaches the value  $v^2$  for large values of v. To justify the factor  $\frac{1}{T}$  recourse would naturally be had to volumetric experiments on superheated steam. Since it has been shown in the previous paper, however, that such experiments do not appear reliable, a more roundabout method is necessitated to justify the factor.

We now proceed to obtain the equations for entropy,  $\eta$ , and energy,  $\epsilon$ . The equations for energy formed by previous writers have all been based on the assumption that either the specific heat at constant pressure or that at constant volume is constant, or on another assumption equally unjustifiable, which will be mentioned later. There will be needed the quantity

$$\psi \equiv \epsilon - T\eta,$$

and since

$$d\epsilon = \mathrm{T}d\eta - pdv,$$

we have

$$d\psi = -\eta d\mathbf{T} - p dv.$$

From this equation follow

$$\left[\frac{\delta\psi}{\delta v}\right]_{\mathrm{T}} = -p \text{ and } \left[\frac{\delta\psi}{\delta \mathrm{T}}\right]_{v} = -\eta.$$

Substituting the value of p from our equation of condition in the first of these, and integrating, there results

$$\psi = -\operatorname{RT}\log_{\varepsilon} (v-a) - \frac{2A}{T\gamma v^{\frac{1}{2}}} + \frac{2A}{T\gamma^{2}}\log_{\varepsilon} \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}} + F(T)$$

where F(T) is some unknown function of T. It should be observed that differences of  $\psi$  at constant temperature formed by means of this equation are more accurate than the value of p found by the equation of condition, for an integral cannot have a greater percentage of error than the integrand.

Making use of the equation

$$\eta = -\frac{\delta\psi}{\delta\mathrm{T}}\Big]_v$$

there is obtained

$$\eta = \operatorname{R} \log_{\varepsilon} (v - a) - \frac{2A}{\gamma T^2} \frac{1}{v^{\frac{1}{2}}} + \frac{2A}{\gamma^{2} T^{2}} \log_{\varepsilon} \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}} - F'(T) \,.$$

It is at once evident that here the factor  $\frac{1}{T}$  in the equation for p plays an important role, and this equation, together with the one to be obtained presently for the energy, may have a great error at small volumes, unless the factor  $\frac{1}{T}$  is justified.

From the equation

$$\epsilon = \psi + T\eta$$

we find

$$\epsilon = -\frac{4A}{\gamma T} v^{\frac{1}{2}} + \frac{4A}{\gamma^2 T} \log \varepsilon \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}} + f(T)$$

where

$$f(\mathbf{T}) = \mathbf{F}(\mathbf{T}) - \mathbf{T} \mathbf{F}'(\mathbf{T}).$$

 $f(\mathbf{T})$ , except for an additive constant, is the kinetic energy, or rather such part of it as depends on the temperature alone.

A number of writers have performed this same integration with their p-v-T equation, and have immediately assumed that  $f(\mathbf{T})$  is linear in the temperature. We are now in position to show that this assumption is contrary to the experimental data at hand by determining  $f(\mathbf{T})$  within certain limits. For, from the equation for  $\epsilon$ , we have

$$f(\mathbf{T}) = \epsilon + \frac{\alpha}{\mathbf{T}v^{\frac{1}{2}}} + \frac{b}{\mathbf{T}} \log_{10} \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}}$$

where, if  $\epsilon$  is expressed in kilogrammeters and v in cubic meters per kilogram, the constants are given by

$$\log a = 6.286713 \qquad \gamma = 1.20484 \,. \\ \log b = 6.567998$$

Now  $\epsilon$  and v are known on the saturation line for values of T from 273°.7 to 473°.7. For there

$$\epsilon = JH - p(v - w)$$

where H is the total heat, J the mechanical equivalent, and w the volume of water at the pressure and temperature under consideration. Consequently f(T) is found for this range.

consideration. Consequently f(T) is found for this range. The values given for the energy on the saturation line by the last equation are untrustworthy at low temperatures, since there v is rather uncertain owing to the error in Regnault's formula for corresponding saturation pressures and temperatures. But from the equation for p, since for the region below 100° C. w is constantly 0.001, there is obtained

$$p(v-w) = \frac{\mathrm{RT}(v-001)}{v-0008} - \frac{\mathrm{A}(v-001)}{\mathrm{T}v^{\frac{3}{2}}(v^{\frac{1}{2}}+\gamma)}$$

In the first term of the second member, since v is large, any error in v cancels out. The last term is so small for the region where serious errors in v may occur that the volumes calculated from the latent heats may be used. This also is true concerning the values of the potential energy; any slight errors in the volumes at low temperatures will not affect things.

In this manner  $\epsilon$  has been calculated for the saturation line, then f(T), and the following table obtained. In the first column is given the absolute temperature, in the second the corresponding value of f(T), and in the third, under f'(T), the average rate of increase of f(T) for each ten degrees.

т	$f(\mathbf{T})$	$f'(\mathbf{T})$	т	$f(\mathbf{T})$	$f'(\mathrm{T})$	т	f(T)	$f'(\mathbf{T})$
273.7	242870		343.7	252135		413.7	261362	
		141.5			126.4			146.6
283.7	244285		353.7	253399		423.7	262828	
		137.3			127.0			151.2
293.7	245658		363.7.	254669		433.7	264340	
		133.4			127.1			155.7
303.7	246992		373.7	255940		443.7	265897	
		131.4			128.5			159.5
313.7	248306		383.7	257225		453.7	267492	
		128.7			133.4			163.3
323.7	249593		393.7	258559		463.7	269125	
		128.0			137.3			165.2
333.7	250873		403.7	259932		473.7	270777	
		126.2			143.0			

Leaving out the lowest temperatures, which will be considered presently, we have the very remarkable fact that f'(T), instead of being constant, as is generally supposed, is an

increasing function of the temperature. Thiesen\* in a recent paper has shown that the total energy, expressed as a function of v and T, is not linear in T, but it has never before been shown, so far as the present writer can discover, that the kinetic energy is not linear, although Massieu+ has given a complicated proof that the specific heat at constant pressure increases with the temperature; this, indeed, was contempo-raneously done by Weyrauch.<sup>‡</sup> Regnault§ has found experimentally the same fact for carbonic acid gas.

This fact that f'(T) is an increasing function of T is so important that it is well to speak of the proof more in detail. We have from page 133

$$f(\mathbf{T}) = \epsilon_s - \pi_s$$

 $\epsilon_s$  and  $\pi_s$  denoting respectively the values of the total and potential energies on the saturation line. At 100° C., 150° C. and 200° C. the values of  $\epsilon_s$  are 254757, 259571 and 264336 respectively, and if the last number were increased by  $49, \epsilon_s$  would be linear in T. On the other hand the corresponding values of  $-\pi_s$  are 1183, 3257 and 6441, the zero of potential energy being that of indefinitely rare gas, and the last exceeds a linear formula for  $\pi_s$  by 1110. Now it is impossible that by any change of *p*-v-T equation, hence a change of the form of  $\pi$ , the number 1110 can be reduced to 49.

We have next a remarkable corroboration of our formulæ, in particular of the factor  $\frac{1}{T}$  in the last term of the *p*-*v*-T equation, by means of Regnault's experimental determination of the specific heat at constant pressure. At temperature 403°.7, pressure 760<sup>mm</sup>, the volume is found by the p-v-T formula to be 1.8018 cubic meters per kilogram. We have then, if Q<sub>1</sub> is the quantity of heat necessary to turn one kilogram of water at 0° C. into this state at constant pressure,

$$\epsilon = JQ_{1} - p(v - w) = JQ_{1} - 18609.$$

But from the formula for  $\epsilon$  on page 133, since we know (page 134) f(403.7) = 259932, we have  $\epsilon = 258909$ , hence  $JQ_1 = 277518$ .

Similarly at temperature 473°.7, pressure 760<sup>mm</sup>, we find the volume to be 2.1314. We thus obtain in the same way

$$JQ_{2} = 292035,$$

 $Q_2$  being the supply of heat necessary to turn one kilogram of water at 0° C. into steam of this second state, at constant pressure.

- \* Wied. Ann., 1897, No. 13. p. 329.
  † Mem. des Savants Étrangers, vol. xxii, p. 58, 1876.
  ‡ Zeitschr. des Ver. Deutsch. Ing., xx, pp. 1, 71, 1876.
- S Mem. of the Institute of France, vol. xxvi, pp. 128, 129.

Accordingly, we find for the mean specific heat at atmospheric pressure from  $403^{\circ}.7$  to  $473^{\circ}.7$ 

$$C_p = \frac{Q_2 - Q_1}{473 \cdot 7 - 403 \cdot 7} = 0.4846$$

or only 0.9 per cent greater than Regnault's mean specific heat at atmospheric pressure from about  $401^{\circ}$ .7 to  $490^{\circ}$ .7, namely 0.4805. When one considers that this deviation could be cancelled by a diminution of less than 0.05 per cent in the latent heat at 200° C., which is far within the limits of error, the essential corroboration of the formulæ is evident.

Gray \* has attempted to show that Regnault's experiments on the specific heat of superheated steam give a value of 0.3787. He does this by comparing the total heat at  $100^{\circ}$  C. with the quantities of heat obtained in the experiments on superheated steam. But this is not allowable, as Regnault + himself distinctly states, and he would not even compare the heats in different series of experiments. In fact if the latter be compared some absurd results are obtained.

We have now to express f(T) by a formula. To get as high a determination as possible the writer has taken Regnault's second determination of the mean specific heat at constant pressure, namely that from 138° C. to 226° C. at atmospheric pressure it is 0.48111. Assuming this to be true from 130° to 230°, we obtain the quantity of heat necessary to heat the steam at atmospheric pressure between those temperatures. Adding this to JQ, found on page 135 we obtain the quantity of heat necessary to heat water at atmospheric pressure from 0° C. into steam at 230° C., JQ<sub>2</sub>. At the latter state the volume is 2.2713, so subtracting p (2.2703) from JQ<sub>2</sub> we find the energy at this state. From the energy formula f(T) is found to be 275278.

It will be noticed that at low temperatures f''(T) apparently changes sign. This is entirely dependent on the formula chosen for total heats at those temperatures. In the preceding article, in forming the expression for the total heats from 0° C. to 100° C.<sub>4</sub> it was assumed that since  $\frac{d^2H}{dt^2}$  was negative above 100°, it was probably so below. Under this assumption we see f''(T) to change sign. On the other hand, if we make f''(T) of one sign throughout, namely positive,  $\frac{d^2H}{dt^2}$  must change sign. Now it is far more probable that the latter does so, for it concerns only a particular set of states, namely those on the

\* Phil. Mag., xiii, p. 337, 1882.

+ Mem. of the Institute of France, vol. xxvi, pp. 165, 166.

saturation line, whereas f''(T) refers to any states whatever. The writer has therefore assumed f(T) to be represented in the range considered, so far as the accuracy of the experiments permits us, by the formula

$$f(\mathbf{T}) = a + b\mathbf{T} + c\mathbf{T}^2$$

Determining a, b and c from the values of f(T) at 273°.7, 373°.7 and 503°.7, there are obtained

a = 215126 log b = 1.902449 log  $c = \overline{2}.894845$ 

How well f(T) is represented by this formula is shown by the following set of values calculated from it, which should be compared with those given on page 134. In order to properly represent the inaccuracies of the formula, in the third column are given the fractional deviations in the latent heats which it would be necessary to assume in order to make the formula absolutely correct.

T  $f(\mathbf{T})$ d | T  $f(\mathbf{T})$ d T  $f(\mathbf{T})$ d 273.7 242870 0 353.7 253200 - 0009 433.7 264536 + 0009 $283\cdot7$  244107 - 0008 363.7 254562 - 0004 443.7 266023 + 0006 293·7 245358 --·0012 373·7 255940 0 453.7 267527 + 0002 $303.7 \ 246626 \ -0015 \ 383.7 \ 257334 \ +0005 \ 463.7 \ 269045 \ -0004$  $313.7 \ 247910 \ -.0017 \ 393.7 \ 258743 \ +.0008 \ 473.7 \ 270580 \ -.0010$  $323.7 \ 249209 \ -.0016 \ 403.7 \ 260167 \ +.0011 \ 503.7 \ 275278$  $333.7 \ 250524 \ -.0014 \ 413.7 \ 261608 \ +.0011$  $343.7 \ 251854 \ -.0013 \ 423.7 \ 263064 \ +.0011$ 

It will be noted that the negative deviations near 313.7 bring the latent heats nearer Griffiths' determinations. It is probable that the latent heats thus calculated from  $f(\mathbf{T})$  as expressed by the formula are from 0° C. to 100° C. nearer the truth than those obtained from the formula for H given in the preceding article.

Theoretically it would be very gratifying if f'(T), which is the specific heat at constant volume for very large volumes, should at low temperatures approach either 3R or  $\frac{5}{2}R$ . These are respectively 141.44 and 117.37. That the first is not approached is evident from the numbers on page 134. Whether or not the second is, is not conclusively shown; the total heats are not accurately enough known at low temperatures to determine this. Since  $\frac{7}{2}R$  would be 165.01, it looks as though in the range say from  $-50^{\circ}$  C. to  $+200^{\circ}$  C. a change in the molecular deportment of the steam occurs, such that the number of degrees of freedom of the molecule increases, and the specific heat at constant volume changes from  $\frac{5}{2}R$  to  $\frac{7}{2}R$ . Such molecular change might explain why a difficulty exists in finding a  $p \cdot p \cdot T$  formula to satisfy both water and steam.

From the relation

$$f(\mathbf{T}) = \mathbf{F}(\mathbf{T}) - \mathbf{T}\mathbf{F}'(\mathbf{T})$$

there follows

$$f'(\mathbf{T}) = -\mathbf{T}\mathbf{F}''(\mathbf{T})$$

from which F'(T) and F(T) are determined. The formulæ for  $\eta$  and  $\psi$  on page 133 become accordingly

$$\begin{split} \eta &= a' \log_{10} (v-a) - \frac{b'}{\mathrm{T}^2 v^{\frac{1}{2}}} + \frac{c'}{\mathrm{T}^2} \log_{10} \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}} + d' \log_{10} \mathrm{T} + \epsilon' \mathrm{T} + \mathrm{K}' \\ \psi &= -a'' \mathrm{T} \log_{10} (v-a) - \frac{b'}{\mathrm{T} v^{\frac{1}{2}}} + \frac{c'}{\mathrm{T}} \log_{10} \frac{v^{\frac{1}{2}} + \gamma}{v^{\frac{1}{2}}} - \\ d' \mathrm{T} \log_{10} \mathrm{T} - e'' \mathrm{T} - \frac{e'}{2} \mathrm{T}^2 + \mathrm{K}'' \end{split}$$

where if  $\eta$  is in kilogrammeters per degree,  $\psi$  in kilogrammeters, and v in cubic meters per kilogram,

$\log a'$	= 2.035657	$\log b' = 5.985683$
$\log c'$	= 6.266968	$\log d' = 2.264662$
$\log e'$	$= \bar{1}$ ·195875	$\log e'' = 2.050449$
$\mathbf{K}'$	= 192.2	K'' = 215126.

These formulæ, with that for the energy, have the same limitations as to pressure and volume as the *p*-v-T formula, and in addition can be used only when T is not far above  $503^{\circ}.7$  or far below  $273^{\circ}.7$ .

The value of K' was determined so as to make the entropy correct for the saturation line at 373°.7; the remaining quantities follow from others previously determined. How well the formula for  $\eta$  represents the saturation line is shown by the following table, in the third column of which are given the fractional changes in the latent heats necessary to make the formula for  $\eta$  correct. These should be the same as those given on page 137, but there are differences, very slight, however.

т	η	d	т	η	d	Т	η	d
273.7	935.4	+.0011	343.7	788.2	0011	413.7	702.5	+.0010
283.7	908.5	0	353.7	773.1	0010	423.7	693.3	+.0011
293.7	883.9	0007	363.7	759.2	- 0006	433.7	684·4	+ .0008
303.7	861.4	0011	373.7	746.3	0	443.7	676.3	+.0008
313.7	840.7	0015	383.7	734.2	+.0002	453.7	668.5	+.0002
323.7	821.7	0015	393.7	722.9	+.0002	463.7	661.3	0002
333.7	804.3	-·0013	403.7	712.4	+.0009	473.7	654.5	0005

It has been remarked that Regnault's formula for corresponding pressures and temperatures is incorrect at low temperatures. Also Wiebe \* has taken exception to his determinations near

\* Zeitschr. für Instrumentenk., xiii, p. 329, 1893.

80° C. There will now be developed a formula for p from the latent heats.

We have from Clausius for the saturation line

$$v - w = \frac{\mathrm{JL}}{\mathrm{T}} \frac{d\mathrm{T}}{dp},$$

from which follows

$$\frac{dp}{pd\mathrm{T}} \equiv \frac{d\log p}{d\mathrm{T}} = \frac{\mathrm{JL}}{\mathrm{T}p \left(v - w\right)}.$$

Let us denote this by D. We have already obtained p(v-w) with great accuracy (page 134) for temperatures below 100° C. For L we take the values from the assumed equation for f(T), which seem to be the best obtainable. Thus D is found for various values of T.

Next the writer has assumed that D is represented by

$$\mathbf{D} = \frac{\mathbf{A}}{\mathbf{T}^2} + \frac{\mathbf{B}}{\mathbf{T}^3} - \frac{\mathbf{C}}{\mathbf{T}^4} \,.$$

This is Rankine's form, with the addition of the term  $\frac{C}{T^*}$ .

Determining A, B and C from the values of D at  $273^{\circ}.7$ ,  $323^{\circ}.7$  and  $373^{\circ}.7$ , there are found

 $\log A = 3.539061$   $\log B = 5.826374$   $\log C = 7.556878$ 

How well this represents D is shown by the following comparison. Under D is given the value as first found from the latent heats, and under D' that according to the formula.

т	D.	$\mathbf{D}'$	T	D	D'
273.7	0.0724625	0.0724626	333.7	0.0462057	0.0462064
283.7	0.0667980	0.0667857	343.7	0.0432180	0.0432188
293-7	0.0617441	0.0617298	353.7	0.0405067	0.0405049
303.7	0.0572187	0.0572100	363.7	0.0380399	0.0380322
313.7	0.0531516	0.0531546	373.7	0.0357738	0.0357738
323.7	0.0495038	0.0495037			

Integrating, there is obtained

$$og_{10} p = -\frac{A'}{T} - \frac{B'}{T^2} + \frac{C'}{T^3} + K$$

where

log 4	<b>Α'</b> =	3.176848	log	$\mathbf{B'}$	=	5.163131
log (	C' =	6.717544	U	K	=	7.844259

K is determined by making p equal to  $760^{\text{mm}}$  when T is  $373^{\circ}$ . In the following table the values of p according to this formula are given in the second column, in the third are Regnault's

pressures,  $p_{\mathbf{x}}$ , in the fourth the fractional deviations of the former from the latter, and in the fifth a few determinations at low temperatures recently made by Juhlin.\*

т	p	<u>р</u> в	d	$p_s$
273.7	4.626	4.6	•006	4.618
283.7	9.277	9.165	.012	9.242
293.7	17.632	17.391	·014	17.46
303.7	31.943	31.548	.013	
31 <b>3</b> ·7	55.449	54.906	.008	
323.7	92.610	91.980	.007	
333.7	149.40	148.79	.006	
343.7	233.59	233.08	.002	
353.7	354.94	354.62	.003	
<b>3</b> 63·7	525.56	525.39	.0003	
373 7	760	760	0	

The variations are considerable, but for those at low temperatures an explanation has already been given, and in the middle of the scale they are not more than could be ascribed to Regnault's not correcting his thermometer to the air-thermometer. Above 100° C. Regnault's gives two formulas, one for temperatures according to the air-thermometer, the other for temperatures by his mercurial thermometer; below 100° this is not done, the inference being that corrections were not made. Now Regnault remarks<sup>+</sup> that at about 50° C. the air-thermometer differs from the mercurial by two-tenths of a degree, which would be sufficient to account for the deviations in that region. The pressures are on the same side of Regnault's as those of Juhlin, and agree well from 80° to 100° with those of Wiebe.

In the following table are given values of various quantities for the saturation line from 0° C. to 100° C. on the basis of the formulæ developed in this paper, and from 100° to 200° from the formulæ adopted in the preceding article. They represent, in the writer's opinion, the best determinations possible with the data at hand. In the first column is given the temperature Centigrade, in the second the heat of the liquid, in the third the total heat, in the fourth the latent heat, in the fifth the pressure, in the sixth the volume, in the seventh the entropy of water,  $\eta_w$ , and in the eighth and ninth the entropy and energy of dry saturated steam,  $\eta_s$  and  $\epsilon_s$ .

\* Beiblaetter zu Wied. Ann., xviii, p. 736.

+ Comptes Rendus, lxix, p. 884, 1869.

t	h	H	Ľ	p	v	$\eta_{w}$	$\eta_8$	88 1
0	0	598.9	598.9	4.626	204.97	0	935.4	242851
10	10.0	602.8	<b>592</b> .8	9.277	105.91	15.5	908 5	244072
20	20.0	606.8	586 8	17.632	57.653	303	883.9	245297
30	30.0	610.7	580.2	31.943	32.861	44.5	861.4	246524
40	40.0	614.6	574.6	55.449	19.518	58.4	840.7	247749
50	50.0	618.5	568.5	92.610	12.032	71.7	821.7	248966
60	60.0	622.3	562.3	149.40	7.6666	84.7	804.3	250168
70	70.0	626.0	556.0	233.59	5.0333	97.3	788.2	251353
80	80.1	629.7	549.6	354.94	3.3953	109.7	773.1	252515
90	90.5	633.3	543.1	525.56	2.3472	121.7	759.2	253652
100	100.4	636.7	536.3	760	1.6587	133.5	746.3	254757
110	110.2	639.8	529.3	1075.4	1.1973	144.9	733.9	255724
120	120.6	642.9	522.3	1491.3	0.88099	156.1	722.6	256691
130	130.7	645.9	$515 \cdot 2$	2030.3	0.65948	167.0	711.9	257649
140	140.9	648.9	508.0	2717.6	0.50152	177.6	702.0	258615
150	151-1	651.9	500.8	3581.2	0.38202	188.0	692.7	259571
160	161 3	654.8	493.5	4651.6	0 30278	198.1	684.0	260517
170	171 6	657.7	486.1	5961.7	0.23985	208.1	675.9	261485
180	181.9	660.2	4786	7546.4	0.19516	2179	668.4	262440
190	192.2	663 3	471.1	9442.7	0.15566	227.5	661.4	263394
200	202.5	666.0	463.5	11689	0.1539	236 9	654.7	264336

The unit here for quantities of heat is the specific heat at 15°, pressures are in millimeters of mercury, volumes in cubic meters per kilogram, energy in kilogrammeters (at Paris) per kilogram, and entropy in kilogrammeters per kilogram per degree.

There is a gratifying confirmation of the formulæ given by Dieterici's experimental determination\* of the volume at 0° C, which was 204.68 cubic meters. This differs from the value given in the table by only a little over one-tenth of one per cent. When one considers the roundabout way in which the latter was found, the agreement is quite remarkable. Dieterici considers his determination to be correct within one-half of one per cent.

There are one or two interesting points which can be brought forward concerning the deportment of steam over ice. At 0° C. that portion of the energy due to the terms in the formula containing v is only nineteen kilogrammeters, which is entirely negligible compared with the latent heat. Hence for steam over ice we can set

$$\epsilon = f(\mathbf{T})$$
.

Now if G is the latent heat of ice, and K its specific heat, we have

$$\epsilon = JL - JK (273 \cdot 7 - T) - JG - p (v - w).$$

Hence

$$JL - JK(2737 - T) - JG - p(v - w) - f(T) = 0.$$
  
\* Wied, Ann., xxxviii, p. 1, 1889.

Below 273°.7 we can set

$$pv = p(v - w) = \operatorname{RT}$$
.

Then, since

$$JL = T(v-w) \frac{dp}{dT} = \frac{Tp(v-w)}{p} \frac{dp}{dT} = RT^{2} \frac{d\log p}{dT}$$

we have

$$\mathrm{RT}^{*} \frac{d \log p}{d\mathrm{T}} - \mathrm{JK} \left( 273 \cdot 7 - \mathrm{T} \right) - \mathrm{JG} - \mathrm{RT} - f(\mathrm{T}) = 0$$

Now first suppose that determinations of L below 0° C. are made, or that those above 0° C. are so accurate that an expression for f(T) is obtained for that region which will bear extrapolation below 0° C. Then  $\frac{d \log p}{dT}$  is known and a relation between p and T determined. Conversely, if the relation between p and T below 0° C. is known, f(T) is at once determined, and thence the latent heats.

- ART. XV. Descriptions of imperfectly known and new Actinians, with critical notes on other species, III; by
   A. E. VERRILL. Brief Contributions to Zoology from the Museum of Yale College, No. LX.
- Family PARACTIDÆ Hertwig, op. cit., 1882. Andres, op. cit., p. 255, 1884. McMurrich, Proc. U. S. Nat. Mus., xvi, p. 160, Jl., 1893.

Paractidæ + Sideractidæ Daniel., 1890.

Paractidæ + Actinostolidæ Carlgren, Kongl. Svenska. Akad. Handl., xxv, II, pp. 64, 137, 1893.

Entacmæous actinaria provided with a mesodermal sphincter musele, but destitute of acontia. Mesenteries usually numerous, nearly always with 12 or more pairs perfect, the number and arrangement not always truly hexamerous. The perfect and larger imperfect mesenteries are usually fertile. Column-wall is usually smooth, sometimes with submarginal plications and solid ridges; rarely with low wart-like elevations or small verucæ, sometimes capable of attaching sand, etc. No actinobranchs. No acrorhagi. No disk-tubercles.

The mesoglea of the wall is usually tough and elastic, thin or thick, often parchment-like or subfibrous, in deep sea forms often thick and coriaceous. Base with an adhesive disk, which is sometimes amplexicaul, embracing permanently the stems of gorgoniæ, etc. Mouth with two siphonoglyphs and numerous lateral folds. Tentacles simple, usually numerous and retractile. Margin generally capable of involution.

This family appears likely to become an extensive one when all the species, whose places in the system are still doubtful, shall have been studied anatomically. At present there is no practical and sure way to distinguish the *Sagartiada* from this family except by the presence of *acontia* in the latter, and this is not always a satisfactory test\* with preserved specimens. However, the thin, smooth, tough, wall is often a fairly good indication of this family, as is also the large number of perfect

<sup>\*</sup> All the acontia may be ejected and lost by violent contractions, when certain Sagartia are placed in preservatives, or they may be easily decomposed in poorly preserved specimens. So they are often not to be found in specimens known to have had them in life. On this account it is doubtful whether several of the genera described by Danielssen, 1890, as destitute of *acontia*, belong to *Paractida* or *Sagartiada*. Of these *Stelidiactis*, *Altantactis*, *Anthosactis*, *Kyathactis*, and *Korenia* are described as having pores or cinclides in the wall (the last has them also in the disk). These genera may, therefore, be sagartians that have lost their acontia. The first three have only 6 pairs of perfect and 'sterile mesenteries, as is often the case in *Sagartiada*; the fourth has 20 perfect pairs; the base is amplexicant. It is *Sideractis* is octamerous, with 16 perfect pairs of very thin mesenteries, partly fertile; tentacles not retractile, 8. Inner ones large; sphincter mesodermal. It probably belongs with *Paractida*.

and fertile mesenteries, which are usually thin and have feeble and diffuse longitudinal muscles.

This family now appears to include Paractis, Stomphia, Actinostola, Actinernus, Actinolobopsis,\* Pycnanthus, ? Sideractis, Cymbactis (near Stomphia), Tealidium, Paranthus, ? Paractiniu, Kadosactis, Phelliopsis, + nov. (type P. Panamensis V. '69), Alloactis, nov. (type A., excavata Hert.), Raphactis, nov., Synanthus Ver., Ammophilactis, nov. (type A., rapiformis Les.).

The last named genus is remarkable for its small base and for having minute adhesive suckers near the margin. It agrees with *Paranthus* in living buried in sand and in its elongated form.

### Raphactis, gen. nov. Type R. nitida V.

Paractidæ having a short column, with thin wall and submarginal longitudinal plications, with raised folds or solid ridges of mesoglea. Sphincter muscle enlarged distally in a thickened portion of the wall, above which the thin wall can be involuted; below this fold the wall may be smooth, or wrinkled, or slightly warty, but without suckers.

Base either broadly expanded, with thin edges, or amplexicaul and embracing permanently stems of gorgoniæ, etc., and in this case the opposite edges of the same or of different individuals unite by sutures.

Tentacles numerous, rather stout, in several rows, retractile. Mesenteries numerous, 12 or more pairs perfect and fertile; some imperfect ones may also be fertile. Stomodæum short. This genus lacks the pores of the disk and wall described in *Korenia*. Synanthus Ver. is closely allied in form and habit; it has a smooth wall and only six pairs of perfect, but fertile, mesenteries.

## Raphactis nitida, sp. nov. Figures 18, 22.

Base large, either broadly expanded, with thin edges, or else clasping stems of sponges, hydroids, etc., and in the latter case the opposite lobes may unite together in a close suture; it secretes a tough thin cuticle. Column in contraction low and broad, most of its surface smooth and white in alcohol, often somewhat glossy or, in others, with a parchment-like appear-The infolded summit is strongly plicated. Toward the ance. contracted summit there is a much thickened fold, usually covered with a series of unequal longitudinally convergent, low, rounded, solid ridges, which vary in number and size, and are

\*This new name is proposed for Actinoloba Hert., 1882 (non Blainv., 1834.) The type is A. reliculata (Dana, sp.) of Patagonia, etc. †This name is proposed for those species of paractids that have been described as Phellia, on account of the adherent cuticle. They have usually 12 or more pairs of perfect, fertile, and very muscular mesenteries.

often lacking or concealed in the smaller examples; in the larger ones about 24 longer, alternating with shorter. Tentacles of moderate size, thick, tapered, blunt, crowded in five or six rows; in the larger specimens sometimes more than 144 in number; the inner are much longer and stouter than the outer ones. The walls of the tentacles are thick, and uniform. In section the column-wall is generally thin, but tough; toward the collar it becomes gradually much thickened and very firm. Sphincter muscle mesogleal, imbedded in the thick collar, large, diffuse, club-shaped distally. Mouth large, with two broad shallow siphonoglyphs and about 12 to 14 distinct folds on each side. The siphonoglyphs may lie in the direction of the short axis of the body, or the reverse. Mesenteries regularly hexamerous, in more than four cycles, the fifth usually more or less incomplete; 12 pairs are perfect and fertile and in the larger specimens 16 pairs may join the stomodæum near its upper end; many of the smaller imperfect ones of the fourth cycle are also fertile; those of the fifth cycle are very small except close to the disk and basal membranes where they become larger and some bear small gonads close to the disk. No acontia were found. The stomodæum is very short and broad, strongly plicated within. The gonads are small; those of the perfect mesenteries are close to the base. Septal foramina of large size occur at about mid-height of the column. Diameter of column of the larger examples, contracted in alcohol, .85 inch (20-22<sup>mm</sup>); of base 1.5 inch  $(36^{\text{mm}})$ ; height of column .75 inch  $(18^{\text{mm}})$ .

Color in life was not noted.

Station 1043, U. S. Fish Com., Str. Albatross, in 130 fathoms off E. coast U. States, latitude of Delaware Bay.

This species has the habit common to many genera and species of deep-sea *Paractidæ* and *Sagartiadæ* of clasping with its base the stalks of hydroids, gorgoniæ, sponges, etc. When the opposite lobes come in contact they unite in a suture.\* So, likewise, do the edges of the bases of adjacent individuals, as shown in fig. 18, A, B, C, and fig. 22.

\* Hertwig made this habit a generic and family character. in the case of Amphianthus and Stephanactis, giving it, undoubtedly, an exaggerated importance, for the same species may live either in this way or attached by a broad base to a shell or stone, as I have repeatedly observed in Actinauge Verrillii McMur. (= nodosa Ver.) and other species. It is even doubtful whether it should be of generic value in any case. Stephanactis was used by me in 1868 for a genus near Discosoma, consequently I propose for the group thus named by Hertwig the new name Stephanauge. It is near Actinauge and Hormathia. The type, Stephanauge abysicola (Moseley, 1877) is identical with my Actinauge nexilis (1883) and came from the same region. S tuberculatu (Hert.) is very similar, if not the same, but it came from the Pacific Ocean, as did S. hydonematis (McMur., 1883), which last is very imperfectly known. The structure of this genus will be discussed later. It differs from Actinauge chiefly in having the thuck wall smooth below the fold, and perforated by distinct cinclides.

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Explanation of cuts.

- FIG. 16.
- Paractis nivea (Less.). Peru,  $\times 1\frac{1}{2}$ . Raphactis Caribæa Ver. on a gorgonian, nat. size, front and side view, contracted. West Indies, 124 fathoms. FIG. 17.
- FIG. 18. Raphactis nitida Ver., three examples, A, B, C, natural size, united together by sutures; contracted in alcohol.

FIG. 19. Sagartia (Psammactis) modesta Ver., 1/2 nat. size, from life, New Haven. Viatrix globulifera D. and M., 1860. FIG. 20.  $\times$  3. Bermuda.

All the drawings are by A. H. Verrill.

Erratum-In No. II of this series, p. 42, I erroneously referred Actinia cruentata Dana to Bunodactis, overlooking the anatomical description of McMurrich (Proc. U. S. Nat. Mus., xvi, p. 150, 1893), under the name Condylactis cruentata. It should, I now believe, be called Actinoides cruentata, as it agrees closely with the typical species of the latter genus. Page 45, Bunodella stelloides. Since, the publication of No. II, I have received from Mr. J. E. Duerden, of Jamaica, larger examples of this species. On dissection they were found to have 24 pairs of per-fect and fertile mesenteries, thus agreeing with *Bunodactis*. The genus *Bunodalla* must, therefore, be dropped, and this species be called *Bunodactis stelloides*. Moreover the name Bunodella had already been used by Matthews for a genus of Eurypteroidea.

## ART. XVI.—A Volumetric Method for the Estimation of Boric Acid; by Louis Cleveland Jones.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXVIII.]

WHEN boric acid and mannite are mixed in solution, a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, and its acid taste is comparable to that of citric acid, much stronger than that of boric acid alone. Magnanini\* has found that the product of such a mixture of boric acid and mannite solutions shows greater electrical conductivity and a lower freezing point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities.<sup>+</sup> Of this reaction between boric acid and the polyatomic alcohols, Thomson, # Barthe, § and Jörgensen | have taken advantage to develop methods for the volumetric estimation of boric acid. Glycerine is used to form a combination with boric acid, sufficiently acidic to give an acid reaction when used with a sensitive indicator and make possible its titration with an alkaline solution. Hönig and Spitz¶ show that in the method of Jörgensen a very large amount of glycerine must be used to prevent the appearance of the indication of alkalinity with phenolphthalein before all the boric acid is neutralized according to the following equation: 2NaOH+B<sub>2</sub>O<sub>2</sub>=2NaOBO+H<sub>2</sub>O-; that in the presence of carbonates the solution must be boiled to decompose bicarbonates and the escape of boric acid by volatilization prevented by the use of a return condenser, and that silica must be removed by the process of Berzelius, and the solution then neutralized by the use of methylorange before a titration of the boric acid can be made.

Vadam,\*\* for the estimation of boric acid in butter, makes use of mannite, which, as he finds, gives sharper indication with litmus than glycerine. According to this process, the solution to be analyzed for boric acid is neutralized by the use of litmus and a solution of sodium hydroxide. Mannite (1-2 grm.) is then added, bringing about an acid reaction with the boric acid present in free condition. The solution is then titrated to alkalinity by sodium hydroxide.

<sup>\*</sup> Gaz. Chim., xx, 428-440, xxi, 134-145.

Klein, J. Pharm. Chim., 4, vol. xxviii; Lambert, Comp. Rend., cviii, 1016–1017. ‡ J. S. C. I., xv, 432. § J. Pharm. Chim., xxix, 163. Zeitschr. f. Angew. Chem., 1897, 5.

Zeitschr. f. Angew. Chem. (1896), 549.

<sup>\*\*</sup> J. Pharm. Chim. (6), viii, 109-111.

None of the above methods with glycerine have, in my experience, given anything but comparatively crude results. The weak acidic properties of boric acid, the interference (and difficulty of removal) of carbondioxide with all organic indicators sufficiently delicate to be used with boric acid, and indeed, the procuring of a standard alkali containing no carbonate, together with the supposed detrimental influence of silica and the lack of a convenient method for its removal, have made the process of Gooch,\* which involves distillation and weighing with calcium oxide, the only means (though requiring long time and exceeding care) in use for the accurate separation and estimation of boric acid. Recently sodium tungstate has been recommended from this laboratory<sup>+</sup> as a substitute for calcium oxide to retain the distilled boric acid. The entire process, however, is one of the most exacting in analytical chemistry, and for this reason a convenient, rapid and at the same time accurate method for the estimation of boron is especially desirable. The first step toward the development of such a process must be the convenient preparation and the accurate estimation of the standard solution of alkali to be used for neutralizing the boric acid. This has been found to be easily accomplished by the process recommended by Küsler.<sup>‡</sup> This observer, in an extensive investigation of the analytical methods for the volumetric estimation of alkalic and alkali carbonates in solution, finds that both phenolphthalein and methylorange are appreciably sensitive to carbonic acid, but when this interfering agent is removed by precipitation with barium chloride according to the process of Winkler, § the remaining free alkali may be estimated with great accuracy by phenolphthalein and decinormal hydrochloric acid.

Obviously, if the difficulties dependent upon the action of carbon dioxide can be obviated, and if the acidity of the boric acid can be increased to such an extent that a sufficiently sensitive indicator will give with accuracy the neutralization point with free alkali, and if the alkali and stronger acid can be combined while boric acid alone remains free, then it should be possible to estimate boric acid volumetrically. Experiment has shown that barium chloride removes carbon dioxide, and that mannite makes a combination with boric acid strongly acidic to phenolphthalein.

<sup>\*</sup> Amer. Chem. Jour., ix, 23-33; Moissan, Comp. Rend., cxvi, 1087: Kraut, Zeitschr. f. Anal. Chem., xxxvi, 165; Montemartini, Gaz. Chim. Ital., xxviii, I, 344.

<sup>+</sup> Gooch and Jones, this Journal, vii, 34.

<sup>&</sup>lt;sup>‡</sup> Zeitschr. f. Anorg. Chem, xiii, 124-150. § Massanalyse.

To obtain the boric acid alone in free condition many attempts have been made. Gladding,\* Thaddeeff+ and Rosenbladt<sup>±</sup> have isolated the boric acid by distillation with methylalcohol and a non-volatile acid. Many indicators theoretically insensible to free boric acid have been used to indicate the neutralization of the stronger acids. Hönig and Spitz,§ and Thomson, use methylorange, Morse and Burton, tropaeolin 00, while Vadam\*\* makes use of litmus. All these indicators, however, have been found by experiment to be more or less affected by boric acid in solution. On the other hand, I have found in the well-known reaction according to which a stronger acid liberates regularly iodine from a mixture of icdide and iodate, the solution of this difficulty. If both the iodide and iodate are in excess of the acid the entire amount of free acid will be neutralized and the corresponding amount of iodine liberated according to the following equation :

### 5KI + KIO3 + 6HCl = 6KCl + 3H<sub>2</sub>O + 3I<sub>2</sub>.

This liberated iodine may be removed by sodium thiosulphate and a solution obtained which is absolutely neutral containing only neutral salts, potassium iodide, iodate and tetrathionate. The statements unade by P. Georgevic<sup>++</sup> and Furry,<sup>++</sup> that boric acid present in moderate amount in solution has not the slightest action on a mixture of iodide and iodate, have been experimentally verified. Therefore when this acid is liberated by an excess of a stronger acid, and the iodine set free destroyed by thiosulphate, it remains free in solution to be titrated in any convenient manner possible.

Following along the lines suggested by the above reactions, a volumetric process for the estimation of boric acid has been developed. For a basis of the investigations, a standard solution of boric acid was prepared by dissolving in a liter of water about eight grm. of carefully weighed anhydrous boric oxide. This anhydrous boric oxide was prepared from the several times recrystallized hydrous boric acid by long-continued fusion over a blast lamp. A solution of approximately  $\frac{n}{5}$  sodium hydroxide was prepared from the ordinary sodium hydroxide of the laboratory. The free alkali

\* Jour. Am Chem. Soc., iv, 568.
† Zeitschr, f. Anal. Chem., xxxvi (9), 568.
† Zeitschr, f. Anal. Chem, xxvi, 18.
§ Zeitschr, f. Anorg. Chem. (18). 549.
[J. S. C. I., xv, 432.
¶ Am. Chem. Jour., x, 154.
\*\* J. Pharm. Chim. (6), viii, 109-111.
+† J. Prac. Chem., xxxviii, 118.
±‡ Am. Chem. Jour. vi, 341.

in this solution was estimated by the process of Winkler recommended by Küsler. The acid used to make this estimation was hydrochloric, standardised by silver nitrate.

The full method for the estimation of boric acid as finally elaborated is as follows: The solution is made clearly acid to litmus by hydrochloric acid and  $5^{\rm cms}$  of a solution (10%) of barium chloride added. An amount of iodate and iodide of potassium sufficient to liberate an amount of iodine at least equivalent to the excess of hydrochloric acid in the acidified solution is mixed with starch in a separate beaker, and the iodine, which is usually thrown out by this mixture, is just bleached by a dilute solution of thiosulphate.

To the now neutral solution of iodide and iodate a single drop of the solution to be analyzed is transferred by a glass If a blue coloration is developed, the solution is acidic rod. with hydrochloric acid, and all the boric acid is in free condition. The amount of iodide and iodate used depends upon the acidity of the solution containing boric acid. Usually 10<sup>cm<sup>3</sup></sup> of a 25 per cent solution of iodide and the same amount of a saturated solution of iodate is sufficient. Any larger excess of hydrochloric acid should be neutralized by sodium hydroxide before the iodide and iodate mixture is added. After the addition of the iodide and iodate solution, containing starch, to the boric acid solution, the liberated iodine should be carefully bleached by thiosulphate. Any excess of thiosulphate in reasonable amount does not seem to be detrimental, but in practice the starch iodide color is clearly bleached, and no more then added. Carbonates prevent a definite indication of the neutral point by thiosulphate and starch iodide, therefore the barium chloride (about 5<sup>cm3</sup>) should be added before this point in the process. The mixture of iodide and iodate is not added to the solution to be analyzed until after it is made acidic, for the reason that when the neutral point is approached by the addition of hydrochloric acid, the starch iodide is thrown out locally by the acid, and the small amount of sodium borate remaining undecomposed does not again bleach the coloration produced, thus obscuring the neutral point which must be obtained before titrating for boric acid.

The solution after the bleaching of the iodine by thiosulphate is colorless and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, and all the borie acid present in uncombined condition. The carbonate lies out of the sphere of action in insoluble form as barium carbonate. A few drops of the indicator, phenolphthalein, are now added, and the alkaline solution run in until a strong red coloration is produced. A pinch of mannite is then added, which bleaches the phenolphthalein coloration, and the alkali solution again

run in to a faint indication, which if permanent on the addition of more mannite, may be taken as the reading point. About 1-2 grm of mannite are necessary for a determination. The boro-mannite compound is sufficiently acidic to liberate iodine abundantly, but it appears to be a time reaction, and at the end of six hours only about 95 per cent of the theoretical amount (considering  $B_2O_3$  as a bivalent acid) has been thrown out. The combination of boric acid and mannite liberates in the presence of iodide and iodate immediately only about onehalf the iodine required on the theory that B<sub>2</sub>O<sub>3</sub> under these conditions acts as a bivalent acid, or with the neutralizing power of metaboric acid, HOBO. When no mannite is present phenolphthaline gives an alkaline indication when only about one-half the amount of alkali theoretically necessary to form the metaborate, NaOBO, has been added. Obviously, then, the starch iodide coloration will not appear at all on the addition of mannite, if about one-half the free boric acid is first neutralized by the solution of alkali, and the remainder of the alkali immediately added to complete neutralization. The point at which the danger of the appearance of the iodide coloration on the addition of mannite has been passed, is roughly indicated before the mannite has been added by the appearance of the strong alkaline indication of phenolphthalein. This indicator would not need to be added at all, if the boromannite compound quickly and regularly liberated iodine from the iodide and iodate. The fact, however, that this compound of boric acid and mannite-as has been ascertained by experiment---liberates, on standing twelve hours, about 99 per cent of the theoretical amount of iodine, places the strength of this acid above that of citric or tartaric acid as investigated by Furry.\* With phenolphthalein, however, the end reaction is sharp and the small amount of carbonate present in the standard solution of alkali is precipitated by the barium chloride already in the solution. The calculation must therefore be based on the amount of free hydroxide in the standard solution of alkali used, according to the following representation:

# $B_{a}O_{a} + 2NaOH = 2NaOBO + H_{a}O.$

The best results and the most definite indications are obtained in cold solution of a volume not greater that  $50^{\text{cm}3}$ . This fact accords with the observations of Magnanini† that the relative electrical conductivity of the boro-mannite solution is decreased by dilution and elevation of the temperature. When silicates are present in solution, the

> \* Am. Chem. Jour., vi, 341. † Gaz. Chim., xx, 428, and xxi, 134.

silicondioxide is liberated by the excess of hydrochloric acid, and this oxide, whether in hydrous or anhydrous condition, neither affects the indication with iodine nor phenolphthalein, nor does it form with mannite a compound of acidic properties. Ammonium salts interfere with the indication given by phenolphthalein and may be removed by boiling with potassium hydroxide in excess, or an indicator used not affected by them.

To test the action of fluorides in the process, several experiments were made in which hydrofluoric acid  $(10^{\text{cm}^3} \text{ of } \frac{n}{10} \text{ solution})$  was introduced into the solution containing salts of sodium, free hydrochloric and boric acids. Barium chloride was then added and the analysis for boric acid completed in the usual way without the accuracy of the results being in any way interfered with by the presence of hydrofluoric acid.

The following table contains the results of a series of analyses in which the boric acid was first drawn into an excess of sodium hydroxide, then estimated according to the method described.

The standard solutions of boric acid used contained I, 7.153 grm. and II, 7.706 grm. per liter. The solution of free sodium hydroxide was 0.21427 normal.

### TABLE I.

		${f B_2O_3}$ Sol. taken. ${f cm^3}$	NaOH Sol. required. cm <sup>3</sup>	B <sub>2</sub> O <sub>3</sub> taken. grm.	${f B_2O_3}\ found.\ grm.$	Errors on B <sub>2</sub> O <sub>3</sub> . grm.
(	((1))	21.95	21.02	0.1571	0.1577	+0.0006
i -	(2)	20.68	19.65	0.1479	0.1474	-0.0002
(	(3)	20.73	19.63	0.1483	0.1473	-0.0010
	(4)	23.02	23.71	0.1776	0.1777	+0.0001
	(5)	23.10	23.80	0.1780	0.1783	+0.0003
<u> </u>	(6)	22.76	23.35	0.1754	0.1750	-0.0004
1	(7)	24.08	· 24·78	0.1855	0.1857	+0.0002
	(8)	22.00	22.50	0.1692	0.1686	-0.0008
	(9)	20.78	21.28	0.1601	0.1595	-0.0006

Practical tests of the method were made upon specimens of crude calcium borate and colemanite.\*

The finely-ground minerals were dissolved in hydrochloric acid and the analyses proceeded with as above described.

\* These specimens were kindly furnished by Dr. C. A. Crampton, of Washington, whom I desire to thank for this courtesy.

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Analysis of crude borate of lime.

	TAI	BLE 11.	
	Ca borate	$B_2O_3$ found.	$B_2O_3$
	taken. grm.	grm.	in %.
(1)	0.4016	0.2289	56.99
(2)	0.4044	0.2302	56.92
(3)	0.4000	0.2285	57.11

# Analysis of Colemanite.

		TABLE III.		
	Mineral taken. grm.	$B_2O_3$ found. grm.	, ≱ B <sub>2</sub> O <sub>3</sub> ,	
(1)	0.4034	0.2064	51.15	
(2)	0.4020	0.2069	50.80	ATORONO
(3)	0.6004	0.3024	50.86	E o o o d
(4)	0.6006	0.3056	50.89	50 99%
(5)	0.2029	0.2592	51.24	
(6)	0.2092	0.2592	50.89	

An analysis for boric acid by this process can be completed in five minutes and the results are obviously accurate within the limits of ordinary analysis. The usually interfering substances, fluorine, silica, and car-bon dioxide, have no detrimental influence on the results of

this process.

## SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. On the Molecular Masses of Gases.—It has been shown by D. BERTHELOT that in consequence of the difference between the coefficients of expansion and compressibility, the molecular masses of gases are proportional, not to the actual density, but to the product of this value into the molecular volume. The molecular volume of a gas is given by the formula  $v_o = v \frac{p}{p_o} [1 + a(p - p_o)] = v \frac{p}{p_o} (1 + ap - ap_o)$ ; in which v is the actual volume under an infinitely small pressure  $p, p_o$  is the normal pressure, and a is a coefficient of the statement of the product of the statement o

tely shall pressure p,  $p_o$  is the normal pressure, and a is a coefficient, constant, according to Regnault between 1 and 6 atmospheres and according to Amagat, below one atmosphere. When  $p_o$  is one atmosphere and p is indefinitely small, the ratio between the molecular volumes of two gases is  $v_o/v_o = (1-a)/(1-a')$ . If their densities be d and d' their molecular masses are proportional to (1-a) d and (1-a') d'. In the table below, the value of a at 0°, the molecular volume  $v_m$  at 0° and one atmosphere, the specific gravity d, oxygen being taken as a standard, the molecular mass M when O = 32 and the atomic mass  $\mu$  when O = 16, are given as calculated :

	Н	N	CO	0
a	- 0.00046	+0.00038	+0.00046	+0.00076
Vm	1.00046	0.99962	0.99954	0.99924
<i>d</i>	0.062865	0.87508	0.87495	1.0
M	2.01472	28.0132	28.0068	32
μ	1.0074	14.002	12.007	16

The author compares the atomic masses of hydrogen, nitrogen, carbon and oxygen deduced as above from the molecular volumes and relative densities, with the best determinations of these values by chemical methods, and shows that they are almost identical.

	0	H	N	C
Physical method,	16	1.0074	14.007	12.007
Chemical method,	16	1.0023 - 1.0075	14.012	12.001 - 12.002

It would appear therefore that not only do the values of the atomic masses obtained from relative density and compressibility confirm the results obtained by chemical methods, but that in some cases they may be taken as the more reliable of the two.— C. R., cxxvi, 954-956, 1030-1033, March, April, 1898. G. F. B.

2. On the Preparation of Metals and Alloys by means of Aluminum. — The commercial production of aluminum on a large scale has rendered it possible to make use of this metal for the reduction of the oxides and chlorides of other metals.

Experiments by GOLDSCHMIDT have greatly improved the earlier processes, by showing that it is not necessary to heat the crucible containing the mixture, from the outside, as in a furnace. It is quite sufficient to inflame this mixture at a single point, from which the action spreads more or less quickly throughout the mass. The ignition may be effected by means of a piece of magnesium wire inserted in the mass and lighted by a match. For mixtures of higher igniting points, a primer made by mixing aluminum powder with a substance easily giving up oxygen, such as lead or manganese peroxide, lead or copper oxide, may be placed on the mixture and this inflamed by the magnesium wire. Since the temperature of the reaction is intense, it is best to line the crucible with a refractory material such as magnesia or alumina, or in some cases the oxide of the metal that is to be reduced. The process may be modified by igniting first a small quantity of the mixture in the crucible, and then adding additional portions from time to time. The metals thus obtained are free from carbon and from carbide, and from aluminum also if the oxide is present in excess. In the case of chromium, the temperature reached was found approximately to be 3000°. The fused chromium thus prepared is permanent even in the air of the laboratory, behaving like a noble metal. Fused manganese resembles bismuth, showing surface colors. By this process, alloys of iron with 20 to 25 per cent of boron and with 40 per cent of titanium have been prepared; and also copper containing 10 per cent of chromium. An alloy of lead and barium decomposes water. Sulphides may be reduced in this way and at a lower temperature. The resulting slag when oxides are used is fused alumina, so hard as scarcely to be scratched by the diamond. In preparing chromium, minute transparent red crystals, resembling rubies, are found in it .- Liebig's Annalen, ccci, 19, June, 1898. G. F. B.

3. On the Electrolytic Preparation of Beryllium.—It has been shown by LEBEAU that beryllium fluoride, while a non-conductor of electricity when fused, becomes a conductor and an electrolyte when mixed with an alkali fluoride. Two beryllium-sodium fluorides, BeF(NaF)<sub>2</sub> and BeF. NaF, are available for this purpose. They are most easily prepared by dissolving beryllium hydrate and sodium carbonate, in the required proportions, in hydrogen fluoride and evaporating. The first of these double chlorides fuses at about  $350^{\circ}$  and the other at about redness. The salt to be reduced is melted in a nickel crucible, acting as the cathode, a rod of graphitic carbon serving as the anode. As soon as the current passes, the external source of heat is withdrawn, the temperature, which should not be allowed to rise above a low red heat, being thereafter maintained electrically. A current of 6 to 7 amperes is required, at an electromotive force of 30 to 40 volts; the metal separating in the crystalline form. If the electrolysis is conducted in a carbon crucible, which contains the other metal in the fused state, and which serves as the anode, alloys of beryllium may be obtained.—C. R., exxvi, 744-746, March, 1898. G. F. B.

4. On Colloidal Silver.-Some experiments have been made by LOTTERMOSER and VON MEYER on the action of various reagents on colloidal silver. They find that acids precipitate it from solution in the "molecular" state, time and dilution being of great To study the influence of time on the change from importance. the colloidal to the molecular condition, a known amount of acid was added to the colloidal solution and the time was observed which was required for the complete change. By placing a drop of the solution on a glass plate resting on white paper, the end of the reaction is easily detected; the time being noted as soon as the separation of fine silver particles can be readily seen. The results of the experiments are given in a table. They show that the less the amount of acid used the longer the time required for the reaction. Moreover, the amount of acid required to produce the change in a given time appears to be inversely as the concentration of the solution. As to the precipitation of colloidal silver by salts of the heavy metals, experiment shows that where reducible metallic chlorides are used there is formed silver chloride and a lower chloride of the metal; a portion of the silver, however, being always precipitated in the insoluble form. If the solution of colloidal silver and of the metallic chloride are both very dilute, it frequently happens that neither silver chloride nor the lower metallic chloride is precipitated, both remaining in solution in the colloidal form. This behavior is particularly shown by mercuric chloride. Neither the chloride, bromide or iodide of colloidal silver appears to have any application in photography, though the iodide is of interest therapeutically. - J. pr. Ch., II, lvi, 241, 1897; lvii, 540, July, 1898. G. F. B.

5. On Silver peroxide and peroxynitrate.—In continuing his researches on the higher oxide of silver and its compounds MULDER has observed that when the substance Ag, NO,, is deprived of an atom of oxygen and the residue is extracted with water, silver nitrate goes into solution and silver peroxide Ag.O. remains. Since the silver nitrate can be extracted in a short time, the nitrate Ag, NO<sub>11</sub> may be regarded as having the composition (Ag<sub>0</sub>O<sub>2</sub>), AgNO<sub>5</sub>. When boiled with water the peroxynitrate is decomposed, oxygen is set free and silver nitrate goes into solution, leaving a residue of silver peroxide. This suggests a convenient method for preparing the peroxide. This higher oxide dissolves in concentrated sulphuric and in concentrated nitric acid, giving brown solutions. The presence of water accelerates the decomposition of these solutions. The peroxide is not soluble in acetic acid though when diluted silver acetate and oxygen are formed. A method for determining the excess of oxygen in the peroxynitrate is described, based on the decomposition of this salt by water. When kept for some time the peroxynitrate undergoes slow spontaneous decomposition even over sulphuric acid. So slow is this change, however, that the author estimates that it

would require about 13 years to eliminate the two atoms of oxygen in excess.—Rev. Trav. Chim., xvii, 129–176, 1898; J. Chem. Soc., lxxiv, ii, 516, Nov. 1898. G. F. B.

6. On Neodymium .- According to BOUDOUARD, neodymium can be isolated by allowing a solution of the pure sulphates of the yttrium metals to remain in contact with potassium sulphate in excess for at least 24 hours, then decomposing the insoluble double sulphate thus produced, with sodium hydrate, dissolving the oxide in nitric acid and precipitating with oxalic acid. The substance thus prepared afforded the atomic mass 143, agreeing well with 142.7 ordinarily assigned to this metal. The oxide is greenish, while the oxalate and anhydrous sulphate are slightly rose-colored. The crystallized sulphate, also rose-colored, while less soluble than the anhydrous sulphate, is more soluble in cold water than in hot. A solution of the sulphate gives an absorption spectrum having a shadow from 591.5 to 584, an intense band from 584 to 572, another from 523 to 519, a feeble band from 512 to 508, and faint bands at 480 and 470, due probably to traces of praseodymium. The double sulphate of potassium and neodymium is more soluble than the corresponding compound of praseodymium.-C. R., cxxvi, 900-901, March, 1898. G. F. B.

7. Leçons de Chimie Physique professées à l'Université de Berlin; par J. H. VAN'T HOFF, Professeur ordinaire à l'Université, etc. Ouvrage traduit de l'allemande par M. Corvisy. Première Partie, La Dynamique Chimique. 8vo, pp. 263. Paris. 1898 (A. Hermann).-The lectures delivered by Professor Van't Hoff during 1897 were upon "Selected subjects in Physical Chemistry" and were divided into three parts, the first comprising Chemical Dynamics, the second Chemical Statics, and the third Relations between the Properties of Substances and their Composition. The present volume contains the first part only; and like all the productions of this eminent authority, is full of the most valuable material admirably classified and clearly treated. The subject is divided into two principal sections, the first on Chemical Equilibrium and the second on Speed of Reaction; each of these being subdivided into two parts, the former section into Chemical Equilibrium in its Physical and especially its Thermodynamic relations and Chemical Equilibrium in its Mechanical and Molecular relations; and the latter section into Theoretical laws of reaction speeds and Experimental results of Reaction speeds. The translator seems to have done his work with care and thus to have made available this excellent presentation of the subject to a much larger class of students. G. F. B.

8. Outlines of Industrial Chemistry ; a Text-book for Students. By FRANK HALL THORP, Ph.D. 8vo, pp. xx, 541. New York, 1898 (The Macmillan Company).—Dr. Thorp has given us in this book a compendium of commercial chemical processes which cannot fail to be of use to the technical student. The first part is devoted to Inorganic industries such as relate to fuels, waters, the soda industry, the chlorine industry, fertilizers, cements, glass and ceramics, pigments, etc. The second part treats of Organic industries, connected with the destructive distillation of wood, bones and coal, with mineral oils, with vegetable and animal oils and soaps, with the sugars and fermentation, with explosives, textiles, etc. The volume is well printed and illustrated. G.F.B.

9. Charge of Electricity carried by the ions produced by  $R \eth ntgen Rays.$ —Mr. C. T. R. Wilson (Phil. Trans. A., 1897, p. 265) has discovered that Röntgen rays can produce a cloudy condensation in dust-free air when the latter is subjected to a sudden expansion. This condensation cannot be produced by expansion without the aid of the rays. Prof. J. J. THOMSON has made use of this phenomenon to determine the value of the product n ev where n is the number of ions in unit volume of the gas, e the charge in an ion, v the mean velocity of the positive and negative ions under a definite electromotive force. The size of the

drops was determined from the expression  $v = \frac{2 g a^2}{9 r}$  in which g

is the acceleration of gravitation; a, the radius of the drop around the ions as nuclei,  $\mu$  the coefficient of viscosity of the gas through which the drops fell. The velocity was determined by observing the time the top layer of the cloud took to fall a given distance.

The mean value of the charge on the ion was found to be  $6.5 \times 10^{-10}$ . The experiments seemed to show that the charge on the ions in hydrogen was the same as in air. From the laws of electrolysis, if *e* is the charge on the hydrogen ion in electrostatic units, *N* the number of molecules in 1 cub. centim. at standard temperature and pressure,

taken as

$$N_e = 129 \times 10^{\circ}.$$
 If e is  

$$0.5 \times 10^{-10}$$

$$N = 20 \times 10^{10}$$

When N deduced from experiments on viscosity of air is  $21 \times 10^{18}$ . The agreement between the value of N got by the kinetic theory of gases by viscosity experiments and the value obtained by Professor Thomson's experiments, leads him to believe that the theory is consistent with the value he has obtained for e, being equal to or of the same order, as the charge carried by the hydrogen ion in electrolysis.—*Phil. Mag.*, Dec. 1898, pp. 528-545.

10. Use of the Coherer in Measuring Electric Waves.—It is still a disputed question whether the coherer can be used in the investigation of stationary electric waves. Professor Murani, of Milan, has published an investigation which seems to show that the coherer is too sensitive to such waves, and that having responded to the first electric impulse it is no longer sensitive to succeeding ones. One thus obtains a more or less constant deflection through a galvanometer in the coherer circuit without any evidence of nodes or ventral segments. O. BEHRENDSEN believes that better results can be obtained by using a comparatively insensitive coherer, which will only respond to the integrated im-
pulses. He makes such a coherer out of comparatively fine carbon powder. By means of such a coherer he obtained evidences of interference phenomena. With a sensitive coherer filled with nickel filings he measured the dimension of electric waves produced by interference in passing through a metallic grating. — Wied. Ann., No. 13, 1898, pp. 1024-1029. J. T.

11. Color Blindness and the Röntgen Rays .- E. DORN has investigated the sensitiveness of the eyes of a totally color-blind person to the Röntgen rays. He believes that the light seen by the color-blind person when the eye is exposed to the rays is not due to a fluorescence excited in the retina by these rays, but is due to a peculiar aptitude of the eyes to perceive these rays. The light excited by the rays is greatest at the periphery of the eye; this indicates that the rods of the eye are sensitive to the Röntgen rays. The author then sought to answer the question whether the cones are also sensitive. He discovered that these are also sensitive and no central blind spot insensitive to these rays could be found in the totally color-blind eye. His experiments he believes can be used to disprove the hypothesis that total color-blindness can be ascribed either to failure or the aptitude of the cones of the eye .- Wied. Ann., No. 13, 1898, pp. 1170-1176. J. T.

12. Regenerating Vacuum Tubes; by W. Rollins. (Communicated.)-In an interesting article in the January number of this Journal on absorption of gases in a high vacuum, Prof. C. C. Hutchins states that after a short period of work the vacuum in a Röntgen tube becomes too high. He then considers the causes of the rise and discusses the various methods for increasing the pressure, recommending oxygen as the most suitable gas because its absorption is slow. The use of oxygen is not new; tubes with adjustable oxygen vacuums were made soon after Röntgen's discovery was announced and were described in a series of notes on Röntgen light in the Electrical Review in 1897-8, and are illustrated in Kirmayer and Oelling's catalogue. In this connection it may be well to state that regenerative tubes with hydrogen vacuums have been recently recommended by Villard, who attaches a closed platinum tube which is heated in a Bunsen flame when it is desired to increase the pressure in the Röntgen tube. A regenerating tube of this kind was described in 1897 in the above-mentioned notes, which was superior to the more recent form, because the hollow platinum tube was used as a target for the impact of the cathode discharge. As this hollow target could be cooled, a large amperage could be used. To increase the pressure it is only necessary to put a drop of liquid hydrocarbon into the hollow target and heat it with the cathode discharge, or illuminating gas can be used, retaining it temporarily in place with a bit of cork.

In some of my experiments I tried a plan used by Professor Trowbridge soon after Röntgen's discovery was announced, but now lost sight of, which consisted in cooling the discharge tube in oil. When this method is applied to a hollow target tube the fresh, cool oil must be made to constantly strike against the back of the target, otherwise this will get red hot and drive back the oil, the hydrogen passing through the platinum. In this way I have had the vacuum change from fifteen inches to one-sixteenth of an inch equivalent air-spark in a short time.

What those of us who are trying to use Röntgen's discovery in medical diagnosis want, is not rediscoveries, but to have placed within our reach apparatus which will convert into Röntgen light an appreciable amount of the energy put into it. At present we may pour in at one end energy at the rate of ten amperes at one hundred volts, and when we come to take it out at the other end as Röntgen radiation there will not be enough with good definition to clearly see through the abdomen. If some broad commercial use could be found for Röntgen's discovery, then the great inventors would attack the problem. At present a tallow candle, notwithstanding its thermic waste, is as a converter of energy into light a shining success compared with the best available Röntgen apparatus. The only notable advance which has been made in practice is due to M. Tesla, but even he seems unable to give much time to this matter; as a result, neither he nor anyone knows when his apparatus will be commercially available. Even when we get it the results will probably be far below the possibilities of the method as shown by the hints dropped from time to time by prominent physicists. Take, for example, Professor Trowbridge's statement that he had made a photograph of the bones of a hand in one-millionth of a second. With the best available apparatus the exposure must be from sixty million to three hundred million times as long. Part of the advance which will be made must consist in devising simple means of making the exciting surges harmonics of the rate of vibration we wish to produce in the radiant energy. All my experiments point in this direction, and I find it practical to get a better result with a small properly-tuned generator than with the largest size improperly adjusted, but I know too little of physics to make any important advance in this matter.

### II. GEOLOGY AND NATURAL HISTORY.

1. The Age of the Earth.—The January number of the Philosophical Magazine contains a notable article by LORD KELVIN, on the age of the earth as an abode fitted for life. This is an extension of the Victoria Institute Annual Address for 1897. The opening pages give an interesting account of the early attitude of the geologist to the subject in demanding almost unlimited time for the geological changes the earth has gone through and for the development of life. Then follows a summary of the arguments by which the author showed (1862 to 1869) the strict limitations of the possible age of earth, viewed as an abode for life, and arrived at the conclusion that the earth's consolidation

could not have taken place less than 20 million, nor more than 400 million years ago. With respect to this he adds:

"During the 35 years which have passed since I gave this wideranged estimate, experimental investigation has supplied much of the knowledge then wanting regarding the thermal properties of rocks to form a closer estimate of the time which has passed since the consolidation of the earth, and we have now good reason for judging that it was more than 20 and less than 40 million years ago; and probably much nearer 20 than 40."

Remarking upon the conclusion reached by Mr. Clarence King (this Journal, Jan., 1893), based largely upon the experimental data supplied by Dr. Carl Barus, in the laboratory of the U. S. Geological Survey, that "we have no warrant for extending the earth's age beyond 24 million of years," he adds that the results of his own recent calculations lead to an estimate not differing much from this.

Going on to discuss the course of events following the first solidification of the earth's surface, the author says :

"§21. I have given strong reasons\* for believing that *immediately* before solidification at the surface, the interior was solid close up to the surface: except comparatively small portions of lava or melted rock among the solid masses of denser solid rock which had sunk through the liquid, and possibly a somewhat large space around the center occupied by platinum, gold, silver, lead, copper, iron, and other dense metals, still remaining liquid under very high pressure."

"§ 22. I wish now to speak to you of depths below the great surface of liquid lava bounding the earth before consolidation; and of mountain heights and ocean depths formed probably a few years after a first emergence of solid rock from the liquid surface (see § 24, below), which must have been quickly followed by complete consolidation all round the globe."...

" $\S 23$ . To prepare for considering consolidation at the surface let us go back to a time (probably not more than twenty years earlier as we shall presently see— $\S 24$ ) when the solid nucleus was covered with liquid lava to a depth of several kilometers; to fix our ideas let us say 40 kilometers (or 4 million centimeters). At this depth in lava, if of specific gravity 2.5, the hydrostatic pressure is 10 tons weight (10 million grammes) per square centimeter, or ten thousand atmospheres approximately. According to the laboratory experiments of Clarence King and Carl Barus<sup>†</sup> on diabase, and the thermodynamic theory<sup>‡</sup> of my brother, the late

\* "On the Secular Cooling of the Earth," vol. iii, Math. and Phys. Papers, §§ 19-33.

† Phil. Mag., 1893, first half-year, p. 306.

<sup>‡</sup> Trans. Roy. Soc. Edinburgh, Jan. 2, 1849; Cambridge and Dublin Mathematical Journal, Nov., 1850. Reprinted in Math. and Phys. Papers (Kelvin), vol. i, p. 156.

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Professor James Thomson, the melting temperature of diabase is  $1170^{\circ}$  C. at ordinary atmospheric pressure, and would be  $1420^{\circ}$  under the pressure of ten thousand atmospheres, if the rise of temperature with pressure followed the law of simple proportion up to so high a pressure."

"§ 24. The temperature of our 40 kilometers deep lava ocean of melted diabase may therefore be taken as but little less than 1420° from surface to bottom. Its surface would radiate heat out into space at some such rate as two (gramme-water) thermal units Centigrade per square centimeter per second.\* Thus, in a year (31<sup>1</sup>/<sub>3</sub> million seconds) 63 million thermal units would be lost per square centimeter from the surface. This is, according to Carl Barus, very nearly equal to the latent heat of fusion abandoned by a million cubic centimeters of melted diabase in solidifying into the glassy condition (pitch-stone) which is assumed when the freezing takes place in the course of a few minutes. But, as found by Sir James Hall in his Edinburgh experimentst of 100 years ago, when more than a few minutes is taken for the freezing, the solid formed is not a glass but a heterogeneous crystalline solid of rough fracture; and if a few hours or days, or any longer time, is taken, the solid formed has the well known rough crystalline structure of basaltic rocks found in all parts of the world. Now Carl Barus finds that basaltic diabase is 14 per cent denser than melted diabase, and 10 per cent denser than the glass produced by quick freezing of the liquid. He gives no data, nor do Rücker and Roberts-Austen, who have also experimented on the thermodynamic properties of melted basalt, give any data, as to the latent heat evolved in the consolidation of liquid lava into rock of basaltic quality. Guessing it as three times the latent heat of fusion of the diabase pitch-stone, I estimate a million cubic centimeters of liquid frozen per square centimeter per centimeter per three years. This would diminish the depth of the liquid at the rate of a million centimeters per three years, or 40 kilometers in twelve years."

"§ 25. Let us now consider in what manner this diminution of depth of the lava ocean must have proceeded, by the freezing of portions of it; all having been at temperatures very little below the assumed 1420° melting temperature of the bottom, when the depth was 40 kilometers. The loss of heat from the white-hot surface (temperatures from 1420° to perhaps 1380° in different parts) at our assumed rate of two (gramme-water Centigrade) thermal units per sq. cm. per sec. produces very rapid cooling of the liquid within a few centimeters of the surface

\* This is a very rough estimate which I have formed from a consideration of J. T. Bottomley's accurate determinations in absolute measure of thermal radiation at temperatures up to 920° C. from platinum wire and from polished and blackened surfaces of various kinds in receivers of air-pumps exhausted down to one tenth-millionth of the atmospheric pressure. Phil. Trans. Roy. Soc., 1887 and 1893.

+ Trans. Roy. Soc. Edinburgh.

(thermal capacity '36 per gramme, according to Barus) and in consequence great downward rushes of this cooled liquid, and upwards of hot liquid, spreading out horizontally in all direc-tions when it reaches the surface. When the sinking liquid gets within perhaps 20 or 10 or 5 kilometers of the bottom, its temperature\* becomes the freezing-point as raised by the increased pressure; or, perhaps more correctly stated, a temperature at which some of its ingredients crystallize out of it. Hence, beginning a few kilometers above the bottom, we have a snow shower of solidified lava or of crystalline flakes, or prisms, or granules of feldspar, mica, hornblende, quartz, and other ingredients: each little crystal gaining mass and falling somewhat faster than the descending liquid around it, till it reaches the bottom. This process goes on until, by the heaping of the granules and crystals on the bottom, our lava ocean becomes silted up to the surface."

"Probable Origin of Granite.- § 26. Upon the suppositions we have hitherto made, we have, at the stage now reached, all round the earth at the same time a red hot or white hot surface of solid granules or crystals with interstices filled by the mother liquor still liquid, but ready to freeze with the slightest cooling. The thermal conductivity of this heterogeneous mass, even before the freezing of the liquid part, is probably nearly the same as that of ordinary solid granite or basalt at a red heat, which is almost certainly somewhat less than the thermal conductivity of igneous rocks at ordinary temperatures. If you wish to see for yourselves how quickly it would cool when wholly solidified, take a large macadamizing stone, and heat it red hot in an ordinary coal fire. Take it out with a pair of tongs and leave it on the hearth, or on a stone slab at a distance from the fire, and you will see that in a minute or two, or perhaps in less than a minute, it cools to below red heat."

"§ 27. Half an hourt after solidification reached up to the surface in any part of the earth, the mother liquor among the granules must have frozen to a depth of several centimeters below the surface and must have cemented together the granules and crystals, and so formed a crust of primeval granite, comparatively cool at its upper surface, and red hot to white hot, but still all solid, a little distance down; becoming thicker and thicker very rapidly at first; and after a few weeks certainly cold enough at its outer surface to be touched by the hand."

\* The temperature of the sinking liquid rock rises in virtue of the increasing pressure : but much less than does the freezing point of the liquid or of some of its ingredients. (See Kelvin, Math. and Phys. Papers, vol. iii, pp. 69, 70.) + Proc. Roy. Soc., May 30, 1895.

‡ Witness the rapid cooling of lava running red hot or white hot from a volcano, and after a few days or weeks presenting a black hard crust strong enough and cool enough to be walked over with impunity.

"Probable Origin of Basaltic Rock."-§ 28. We have hitherto left, without much consideration, the mother liquor among the crystalline granules at all depths below the bottom of our shoaling lava ocean. It was probably this interstitial mother liquor that was destined to form the basaltic rock of future geological time. Whatever be the shapes and sizes of the solid grauules when first falling to the bottom, they must have lain in loose heaps with a somewhat large proportion of space occupied by liquid among them. But, at considerable distances down in the heap, the weight of the superincumbent granules must tend to crush corners and edges into fine powder. If the snow shower had taken place in air we may feel pretty sure (even with the slight knowledge which we have of the hardness of the crystals of feldspar, mica and hornblende, and of the solid granules of quartz) that, at a depth of 10 kilometers, enough of matter from the corners and edges of the granules of different kinds, would have been crushed into powder of various degrees of fineness, to leave an exceedingly small proportionate volume of air in the interstices between the solid fragments. But in reality the effective weight of each solid particle, buoyed as it was by hydrostatic pressure of a liquid less dense than itself by not more than 20 or 15 or 10 per cent, cannot have been more than from about onefifth to one-tenth of its weight in air, and therefore the same degree of crushing effect as would have been experienced at 10 kilometers with air in the interstices, must have been experienced only at depths of from 50 to 100 kilometers below the level of the lava ocean."

"§ 29. A result of this tremendous crushing together of the solid granules must have been to press out the liquid from among them, as water from a sponge, and cause it to pass upwards through the less and less closely packed heaps of solid particles, and out into the lava ocean above the heap. But, on account of

\* NOTE BY THE EDITOR: An Addendum at the close of the paper quotes the following determination of melting points by Prof. Roberts-Austen:

	Melting-point.	Error.
Feldspar	1520° C.	$\pm 30^{\circ}$
Hornblende	about 1400°	
Mica	1440°	$\pm 30^{\circ}$
Quartz	1775°	$\pm 15^{\circ}$
Basalt	about 880°	

The author adds:

"These results are in conformity with what I have said in §§ 26-28 on the probable origin of granite and basalt, as they show that basalt melts at a much lower temperature than feldspar, hornblende, mica, or quartz, the crystalline ingredients of granita. In the electrolytic process for producing alumina, on which the melting-point is certainly above 1700° C. or 1800° C, is dissolved in a bath of melted cryolite at a temperature of about 800° C. So we may imagine melted basalt to be a solvent for feldspar, hornblende, mica, and quartz at temperatures much below their own separate melting-points; and we can understand how the basaltic rocks of the earth may have resulted from the solidification of the mother liquor from which the crystalline ingredients of granite have been deposited." the great resistance against the liquid permeating upwards 30 or 40 kilometers through interstices among the solid granules, this process must have gone on somewhat slowly; and, during all the time of the shoaling of the larva ocean, there may have been a considerable proportion of the whole volume occupied by the mother liquor among the solid granules, down to even as low as 50 or 100 kilometers below the top of the heap, or bottom of the ocean, at each instant. When consolidation reached the surface, the oozing upwards of the mother liquor must have been still going on to some degree. Thus, probably for a few years after the first consolidation at the surface not probably for as long as one hundred years, the settlement of the solid structure by mere mechanical crushing of the corners and edges of solid granules, may have continued to cause the oozing upwards of mother liquor to the surface through cracks in the first formed granite crust and through fresh cracks in basaltic crust subsequently formed above it."

After a further discussion of the probable origin of continents and ocean depths, and also of the earth's atmosphere, the author concludes as follows:

"43. Whatever may have been the true history of our atmosphere it seems certain that if sunlight was ready, the earth was ready, both for vegetable and animal life, if not within a century, at all events within a few hundred centuries after the rocky consolidation of its surface. But was the sun ready? The well founded dynamical theory of the sun's heat carefully worked out and discussed by Helmholtz, Newcomb, and myself," says NO if the consolidation of the earth took place as long ago as 50 million years; the solid earth must in that case have waited 20 or 50 million years for the sun to be anything nearly as warm as he is at present. If the consolidation of the earth was finished 20 or 25 million years ago, the sun was probably ready,—though probably not then quite so warm as at present, yet warm enough to support some kind of vegetable and animal life on the earth."

"§ 44. My task has been rigorously confined to what, humanly speaking, we may call the fortuitous concourse of atoms, in the preparation of the earth as an abode fitted for life, except in so far as I have referred to vegetation, as possibly having been concerned in the preparation of an atmosphere suitable for animal life as we now have it. Mathematics and dynamics fail us when we contemplate the earth, fitted for life but lifeless, and try to imagine the commencement of life upon it. This certainly did not take place by any action of chemistry, or electricity, or crystalline grouping of molecules under the influence of force, or by any possible kind of fortuitous concourse of atoms. We must pause, face to face with the mystery and miracle of the creation of living creatures."

\* See "Popular Lectures and Addresses," vol. i, pp. 376-429, particularly page 397.

2. Recent Publications of the U. S. Geological Survey:\* ANNUAL REPORTS.—The five parts (making 6 volumes) of the 18th Annual Report are now complete. All have been noticed excepting the following papers included in parts II and III:

The Triassic Formations of Connecticut, by W. M. Davis. Pt. II, pp. 1 to 192, 20 pls. including folded map and sections.

Geology of the Edwards Plateau and Rio Grande Plain adjacent to Austin and San Antonio, Texas, with reference to the occurrence of underground waters, by R. T. Hill and T. W. Vaughan. Pt. II, pp. 193-321, pls. 31.

Vaughan. Pt. II, pp. 193-321, pls. 31. A Table of the North American Tertiary Horizons, correlated with one another and with those of Western Europe, with annotations, by W. H. Dall. Pt. II, pp. 323 to 348. Glaciers of Mount Rainier, by I. C. Russell, with a paper on

Glaciers of Mount Rainier, by I. C. Russell, with a paper on The Rocks of Mount Rainier, by G. O. Smith. Pt. II, pp. 349 to 423, pls. 18.

The Age of the Franklin White Limestone of Sussex County, New Jersey, by J. E. Wolff and A. H. Brooks. Pt. II, pp. 425 to 457, with geological map. A Geological Sketch of San Clemente Island, by W. S. T.

A Geological Sketch of San Clemente Island, by W. S. T. Smith. Pt. II, pp. 459 to 496, pls. 13.

Geology of the Cape Cod District, by N. S. Shaler. Pt. II, pp. 497 to 593, pls. 8.

Recent Earth Movement in the Great Lakes Region, by G. K. Gilbert. Pt. II, pp. 595 to 647, pl. 1.

Gilbert. Pt. II, pp. 595 to 647, pl. 1. Some Coal Fields of Puget Sound, by Bailey Willis. Pt. III, pp. 393 to 436, 17 pls.

Geology and Mineral Resources of the Judith Mountains of Montana, by W. H. Weed and L. V. Pirsson. Pt. III, pp. 439 to 616, 18 pls. including maps. See this Journal, vol. vi, p. 508, December, 1898.

The Mining Districts of the Idaho Basin and the Boise Ridge, Idaho, by Waldemar Lindgren, with a report on fossil plants by F. H. Knowlton. Pt. III, pp. 619 to 794, pls. 16.

F. H. Knowlton. Pt. III, pp. 619 to 794, pls. 16. Preliminary Report on the Mining Industries of the Telluride Quadrangle, Colorado, by C. W. Purington. Pt. III, pp. 745 to 850. The areal geology of this quadrangle is given by Mr. Cross in plate cili.

The Nineteenth Annual Report (1897-98) will appear in six parts (seven volumes). The report of the Director C. D. Walcott of Part I, pp. 143 with two folded maps, giving an account of the operations of the Survey to June 30, 1898, is already issued. The total appropriation for the work of the Survey was 1,033,963.60. Besides continuing the work already begun along essentially the same lines, this increased appropriation provided for the Survey of Forest Reserves, the boundary line between Idaho and Montana and the extension of work in Alaska. Mineral Resources for

\* Issued since March, 1898. For last complete list and references to earlier ones see this Journal for April, 1898, p. 303; notices published since this date are referred to under the respective titles. 1897, forming Part VI of the Nineteenth Annual Report, will appear in two volumes; the first including Metallic Products, Coal and Coke, the second, Non-Metallic Products excepting Coal and Coke. Separates are nearly all issued and volumes will soon appear.

MONOGRAPHS: Fossil Medusæ Mon. xxx, by C. D. Walcott, pp. 201, pls. 47. See this Journal, December, 1898, p. 508.

BULLETINS: The Cretaceous Foraminifera of New Jersey, by R. M. Bagg, Jr. Bull. No. 88, pp. 89, pls. 6.

Some Lava Flows of the Western Slope of the Sierra Nevada, California, by F. L. Ransome, Bull. 89, pp. 73. See this Journal for December, 1898, p. 509.

Bibliography and Index of North American Geology, Paleontology, Petrology and Mineralogy, by F. B. Weeks, Bull. No. 149, pp. 152, for 1896; Bull. 156, pp. 130, for 1897.

The Educational Series of Rock Specimens collected and distributed by the U. S. Geological Survey, by J. S. Diller, Bull. 150, pp. 400, pls. 47. See this Journal, January, 1899, p. 74.

The Lower Cretaceous Gryphæas of the Texas Region, by R. T. Hill and T. W. Vaughan, Bull. No. 151, pp. 138, pls. 35. See this Journal, January, 1899, p. 70.

A Catalogue of Cretaceous and Tertiary Plants of North America, by F. H. Knowlton, Bull. 152, pp. 247.

A Bibliographic Index of North American Carboniferous Invertebrates, by Stuart Wheeler, Bull. No. 153, pp. 653.

A Gazetteer of Kansas, by Henry Gannett, Bull. No. 154, pp. 246, with map of the State.

Earthquakes in California in 1896 and 1897, by C. D. Perrine, Bull. 155, pp. 45.

WATER SUPPLY AND IRRIGATION PAPERS: No. 12, Underground Waters of a portion of Southeastern Nebraska, by N. H. Darton, pp. 56, pls. 21.

No. 13, Irrigation Systems in Texas, by W. F. Hutson, pp. 68, pls. 10.

No. 14, Tests of Pumps and Water Lifts, by O. P. Hood, pp. 91, pl. 1.

Nos. 15 and 16, Operations at River Stations in 1897, Parts I and II, by F. H. Newell, pp. 200.

No. 17, Irrigation near Bakerfield, California, by C. E. Grunsky, pp. 96, pls. 16.

No. 18, Irrigation near Fresno, California, by C. E. Grunsky, pp. 94, pls. 14.

Geologic Folios: No. 38, Butte Special, Montana, Long. 112° 29' 30" to 112° 36' 42", Lat. 45° 39' 28" to 46° 02' 54", by S. F. Emmons and G. W. Tower, Jr.

No. 39, Truckee, California, Long. 120° to 120° 30', Lat. 39° to 39° 30', by Waldemar Lindgren.

No. 40, Wartburg, Tennessee, Long.  $84^{\circ}$  30' to  $85^{\circ}$ , Lat.  $36^{\circ}$  to  $36^{\circ}$  30', by Arthur Keith.

No. 41, Sonora, California, Long. 120° to 120° 30', Lat. 37° 30' to 38°, by H. W. Turner and F. L. Ransome. No. 42, Neuces, Texas, Long. 100° to 100° 30', Lat. 29° 30' to 30°, by R. T. Hill and T. W. Vaughan.

No. 43, Bidwell Bar, California, Long. 121° to 121° 30', Lat. 39° 30' to 40°, by H. W. Turner.

No. 44, Tazwell, West Virginia, Long. 81° 30' to 82°, Lat. 37° to 37° 30', by M. R. Campbell. No. 45, Boise, Idaho, Long. 116° to 116° 30', Lat. 43° 30' to

44°, by Waldemar Lindgren.

No. 46, Richmond, Kentucky, Long. 84° to 84° 30', Lat. 37° 30' to 38°, by M. R. Campbell.

Topographic Folios: Physiographic Types by Henry Gannett. See this Journal for July, 1898, p. 102. J. S. D.

3. A Catalogue of the Cretaceous and Tertiary plants of North America; by F. H. KNOWLTON, pp. 1-247, 1898, U. S. Geological Survey, Bulletin 152 .- Mr. Knowlton has furnished paleobotanists a valuable aid to study by publishing this working catalogue of the known American species of Cretaceous and Tertiary plants, without waiting to make it absolutely perfect. Systematic names are checked back as far as the Kew Index for genera found also living, and to original source of description for species and the more important references to later descriptions or illustrations. Also the matters of geographical distribution and geological range are given so far as commonly reported in the literature, while the full knowledge regarding these points is left for future investigation. The Bibliography is a list of the papers consulted without assuming that it is a complete list.

4. Iowa Geological Survey. Annual Report, 1897, with accompanying papers. SAMUEL CALVIN, State Geologist, vol. viii, pp. 1-427, plates 1-xxxii, figures 1-13, and six maps, 1898.-This eighth volume contains detailed reports of the areal geology and, where ascertained, the faunal lists of fossil species for the counties of Dallas, Delaware, Buchanan, Decatur and Plymouth, with excellent colored maps and frequent half-tone views of important rock sections and landscapes. H. F. Bain contributes a chapter on Properties and Tests of Iowa Building stones. H. S. W.

5. A Preliminary Report on a Part of the Gold Deposits of Georgia; by W. S. YEATES, State Geologist, and S. W. McCallie and FRANCIS P. KING, Assistant Geologists. 1896. Geological Survey of Georgia, W. S. Yeates, State Geologist. Bulletin No. 4-A.-This handsome and well illustrated volume of 542 pages gives an account of the various gold deposits of Georgia, especially with reference to their present development. As is well known, these lie chiefly on lines running northeast and southwest, in the northern part of the State. Some fifty years since, the amount of gold annually coined at the State mint amounted to nearly or quite \$500,000; but since the exhaustion of the placer mines, from which most of the gold had been derived, the output has fallen off very largely, and in 1895 the total production of

168

gold (and silver) is estimated as but \$128,000. The geologist, however, expresses the opinion that with the deep-mining and economic working of refractory ores now being introduced, the future outlook is promising, and the production may be expected to reach what it was in former years.

6. The Report of the Governor of Arizona to the Secretary of the Interior, for the fiscal year ending June 30th, 1898.—This report, in addition to the discussion of various economic and agricultural subjects of importance especially to the community involved, contains also a detailed account of the distribution of the metallic wealth of the Territory, by W. P. Blake, Territorial Geologist. How varied and extensive the metallic products of Arizona are, is well understood, and this fact gives much interest to this account of the various gold fields, the mines of silver and argentiferous lead, of copper not the least important of the metals, also coal, marble and other mineral products. It is interesting to note that the production of copper in Arizona has been increased fourfold since 1883, and for the first six months of 1898, amounted to nearly 20 per cent of the entire production of the United States.

7. Die natürlichen Pflanzenfamilien, Lieferung 182, 183, Leipzig, 1898.—Professor ENGLER has carried this important work nearly to completion. The present installments comprise a portion of one of the indexes; a general index is to follow at the close. Certain of the groups of Cryptogams are still in arrears, but they cannot be much longer delayed. The wealth of illustrations, the general treatment of orders, and the skill with which minor references to distribution and use have been employed, make the whole work a treasury for general and special botanists. Under the conditions of publication, it was impossible to avoid the unfortunate separation of subjects which should have been united, but these annoyances are now likely to be forgotten by all the patient subscribers. There cannot be one of these subscribers who does not feel that he has obtained far more than the worth of his money in these clearly printed and attractive volumes.

G. L. G. 8. The Fishes of North and Middle America. A descriptive catalogue of the species of fish-like vetebrates found in the waters of North America, north of the Isthmus of Panama; by DAVID STARE JORDAN and BARTON WARREN EVERMANN. Part III, pp. i-xxiv, 2183-3136. Washington, 1898 (Smithsonian Institution: Bulletin of the U. S. National Museum, No. 47).—The third part of this exhaustive Memoir on the Fishes of North America, mentioned on page 79 of the last number, has now appeared. Pages 2183 to 2873 are devoted to the description of species, and the remainder of the volume is given to a key to the families of the true fishes or Teleostei, the glossary of technical terms and the index.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Ostwald's Klassiker der Exakten Wissenschaften.-The latest additions to this valuable series of scientific classics are Nos. 97 to 103, whose titles are given below. We have often had occasion to call attention to this series before, and its value must now be well appreciated by all of those interested in physics and physical work. It would be difficult to overestimate the importance to the physical student of having before him such papers as are here brought together. They are all of the highest character, and a large part of them, as originally published, are com-paratively inaccessible; but they are here republished in convenient form, ready for the student in his study, or the worker in the laboratory. Space forbids any separate notice of the indi-vidual memoirs here mentioned, and indeed this is unnecessary, since they are too well known to require it. Ostwald's Series gains additional interest from the fact that an undertaking on somewhat similar lines is being carried forward in this country (already noticed in this Journal), as Harper's Scientific Memoirs, edited by Professor Ames of Baltimore.

Nr. 97. Sir Isaac Newton's Optik oder Abhandlung über Spiegelungen, Brechungen, Beugungen und Farben des Lichts. (1704) II und III Buch.

Nr. 98. Ueber das Benzin und die Verbindungen desselben. Von Eilhard Mitscherlich. (1834.)

Nr. 99. Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen. Von R. Clausius. (1850.)

Nr. 100. Abhandlungen über Emission und Absorption von G. Kirchhoff.

I. Ueber die Fraunhofer'schen Linien. (1859.) I. Ueber den Zusammenhang zwischen Emission und Absorption von Licht II.

und Wärme (1859.) III. Ueber das Verhältniss zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht (1860-1862.)

Nr. 101. Abhandlungen über Mechanische Wärmetheorie von G. Kirchhoff.

I. Ueber einen Satz der mechanischen Wärmetheorie und einige Anwendungen desselben. (1858.)

II. Bemerkung über die Spannung des Wasserdampfes bei Temperaturen die dem Eispunkte nahe sind. (1858.)

III. Ueber die Spannung des Dampfes von Mischungen aus Wasser und Schwefelsäure. (1858.)

Nr. 102. Ueber physikalische Kraftlinien. Von James Clerk Maxwell. Nr. 103. Joseph Louis Lagrange's Zusätze zu Eulers Elementen der Algebra. Unbestimmte Analysis.

2. University of Tennessee Record of Scientific Engineering. Published by the University of Tennessee Press, Knoxville, Tennessee.-Number 7 of this publication, for November, 1898, pp. 343-405, has been recently received. It contains a number of original scientific papers, and gives evidence of the scientific activity at the University of Tennessee. Among the papers we notice one on Nutrition Investigations, by Charles E. Wait; several papers on Chemical Analytical Methods; another on Meteorological Observations by means of Kites, by W. M. Fulton; also, Notes on the Flora of West Tennessee, by S. M. Bain.

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### FOURTH SERIES.

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### ΤΗΕ

# AMERICAN JOURNAL OF SCIENCE

### [FOURTH SERIES.]

ART. XVII.—Studies in the Cyperaceæ; by THEO. HOLM. IX. The genus Lipocarpha R.Br. With nine figures in the text, drawn by author.

THE genus Lipocarpha was established by Robert Brown upon some plants, which were formerly enumerated by Vahl as species of Hypelyptum. This latter generic name was, however, a corruption of "Hypolytrum" a genus of Richard, and since Vahl had included certain species under this, which did not exhibit the generic character of Hypolytrum as understood by Richard, Robert Brown transferred these to his new genus Lipocarpha: L. argentea, L. sphacelata and L. filiformis.

As regards the derivation of the name Lipocarpha, this is not, as stated by American authors, derived from " $\lambda \ell \pi \sigma \sigma$  fat and  $\kappa d \rho \phi \sigma$  chaff, from the thickness of the inner scales of some species," but from " $\lambda \ell \pi \sigma$  fall off, drop," "from the whole of its squame being deciduous" as already stated by Robert Brown in the Botany of Congo; furthermore the inner scales are never "fat" but constantly membranaceous in the species of Lipocarpha, hitherto known. Lipocarpha is a small genus, containing only seven species according to Bentham and Hooker, six of which are described by Bœckeler; in later years four more species have been recorded from West Africa by Ridley. While the genus is chiefly tropical, L maculata extends as far north as Virginia, and L. Sellowiana as far south as Buenos Ayres. The habit of the species is much the same, reminding one of Kyllinga, and they seem to prefer damp or periodically inundated ground. Considered

AM. JOUR. SCI.—FOURTH SERIES, VOL. VII, NO. 39.—MARCH, 1899.

from a morphological view point, our genus possesses a main inflorescence composed of a few short and almost roundish spikes, surrounded by long, green involucral leaves. Each spike bears a number of spirally arranged bracts, inside of which are two minute, membranaceous scales, which surround The position of these inner scales is somewhat a flower. singular, being mediane, the lowest one being situated on the posterior face of rhacheola, the upper one on the anterior face or a little distance above the supporting bract. Both of these scales are hyaline, nearly equal in length and apparently of the same shape, but only the anterior supports a flower. The question is then to decide whether we have "a one-flowered spikelet" or "a single flower" before us, and this is a point that has always been so much disputed.

It would seem most natural, however, to define the two scales and the flower as constituting a one-flowered spikelet, wherein the lower scale would represent the prophyllon of the rhacheola and the upper one the bract of the flower. The position of the lower scale corresponds exactly with that of a true prophyllon in other *Cyperaceæ*. Furthermore its anatomical structure shows us two prominent stereome-bundles and a distinct bicarinate outline, in contrast to the upper scale, the bract, in which we have observed a mediane mestome-bundle,



FIG. 1. Diagram of spikelet of *L. maculata*. Explanation in the text.

corresponding with other bracts. The accompanying diagram of a spikelet of L. maculata shows us the supporting bract (B), in the axil of which is developed a rhacheola with a dorsal prophyllon (P) and a bract (b), which supports the naked flower. This explanation seems to us the most natural, when we consider the minor inflorescences of other Cyperaceæ, where the rhacheola is often provided with a basal, empty prophyllon, bicarinate or tubular as in

Carex, Cyperus, Dulichium, Fuirena and others. Although Robert Brown did not define the lower scale as a prophyllon, he considered, at least in his Botany of Congo,\* the minor inflorescence of Lipocarpha as a spikelet, not as a single flower, a suggestion that was, also, followed by Kunth, Torrey, Bœckeler and apparently by Baillon. Other authors have held the opinion that there is "a single flower" instead of a spikelet, for instance: Vahl, Nees von Esenbeck, Liebmann, Michaux, Bentham, Ridley, Gray, Schumann, Pax and Goebel. Pax describes the flower as possessing two prophylla: "eine hermaphrodite mit zwei medianen Vorblättern versehene

\* For references consult the bibliography appended to this article.

Blüte," while Goebel, in his interesting paper on some *Cyperaceae* from Java, considers the flower as possessing only one prophyllon, but is uncertain as to the definition of the other scale: "Jede Blüte besitzt zwei Schuppen, das eine derselben wird als Vorblatt zu bezeichnen, das andere ist mir unklar geblieben."

As regards the flower itself, we have noticed only one stamen in L. maculata and two, seldom three stigmata; purely pistillate flowers with rudiments of a stamen were, also, observed. In this respect L. maculata agrees with L. argentea, as described by Goebel, with the exception that the anther of the stamen in this last species was observed to be two-celled instead of four-celled, as we invariably noticed in L. maculata and L. microcephala. Concerning the systematic position of our genus with its "mediane scales" and "one-flowered spikelets," it seems that Robert Brown was justified in separating it from Richard's Hypolytrum, the flower of which is generally described as possessing "two lateral prophylla." It is difficult at present to point out the nearest allies to our genus, con-sidering that it shows some affinities to Hemicarpha, as suggested by Pax in his treatment of this group for Engler's and Prantl's work upon the natural families. Further researches on the morphological structure of the other genera may possibly assist us in determining its correct place within the order, especially when combined with such peculiarities as may be observed in the anatomical structure. In this last respect Lipocarpha is very interesting, and in order to make our study as complete as possible, we shall briefly discuss some of the most important features, which we have observed in L. maculata Kth. from subtropical Florida, L. argentea R.Br. from Nilagiri in Eastern India and Hongkong, L. sphacelata R.Br. from the Isthmus of Panama and L. microcephala Kth. from Japan.

### The stem above ground,

the scape, is cylindrical and more or less furrowed in the species examined. The enticle is thin and perfectly smooth. The epidermis is here developed into several strata (from two to four) between the subepidermal bundles of stereome. A considerable variation is to be noticed in the outer epidermis, as regards the thickening of the outer cell-walls and the lumen of the individual cells. Thus we find a strongly thickened epidermis in *L. argentea*, but one with very thin walls in *L. microcephala*. The epidermis-cells above the stereome are usually smaller than those surrounding, and contain the characteristic silicious cones, which we have often described in our previous papers on this order. These cone-bearing cells are

thin-walled in L. maculata and form a projection in the shape



FIG. 2. A cone-cell above the stereome from epidermis of the stem of *L. maculata*.  $\times 400.$ 

of a minute papilla (fig. 2), while no other epidermal projections were observed in any of the species examined. The outer epidermis-cells, which lie between the stereomebundles, are very large and round in transverse sections except in *L. argentea*, in which the radial walls have become stretched so as to render the lumen narrow. It is, also, to be noted that the epidermis in *L. argentea* forms very prominent ribs on each

side of deep furrows in which the stereome is located. Similar, but more shallow, furrows are also noticeable in L. maculata and L. sphacelata above the stereome. In L. microcephala, however, furrows are, also, present, but the adjoining projecting ribs are not here due to the increased size of epidermis, but to the stereome. These species of *Lipocarpha* thus illustrate a singular variation regarding the location of the stereome: being situated in furrows as in L. maculata, L. sphacelata and L. argentea, or in the projecting ribs in L. microcephala. The presence of similar furrows in the stem has, also, been mentioned by Rikli in Ficinia, Fuirena, Heleocharis and others; the stereome, according to this author, is located in furrows in Heleocharis geniculata R.Br. and Fuirena, but located in the projecting ribs in Ficinia stolonifera Nees and F. tenuifolia The interior layers of epidermis show a very uniform Kth. structure and the walls are very thin. Stomata are present and form longitudinal rows between the stereome-bundles: they are slightly projecting and the air-chamber is deep and narrow. In this manner they are freely exposed in our species with the exception of L. microcephala, where they occupy the deep furrows between the projecting bundles of stereome.

As regards the mechanical tissue, the stereome, this is very well represented in the stem of our species, forming relatively large bundles on the leptome-side of the outer mestome-bundles or on the hadrome-side of the inner ones. In the first case the stereome-bundles are situated immediately underneath the epidermis and border inwards on the chlorophyll bearing palisade-sheath, that surrounds the mestome-bundles. It is generally thick-walled in our species, especially in *L. argentea* and *L. sphacelata*. When considered in transverse sections, the stereome forms roundish groups on the leptome-side of the peripherical mestome-bundles, where it is usually thick-walled; the stereome, that supports the inner mestome-bundles, is, on the other hand, thin walled and forms an arch around the hadrome of each bundle. *Lipocarpha* thus possesses a well developed stereome, which accompanies the mestome-bundles, but without developing as a continuous ring outside or between these bundles.

In proceeding to examine the assimilating tissue of the stem, we notice in Lipocarpha a structure which is very different from that of other genera, discussed in our former papers: Carex, Dulichium, Fuirena, Dichromena and Scleria.\* This divergence consists in the very regular arrangement of the palisade-cells radially around the peripherical mestome-bundles. In the other genera, previously described, the palisade-cells were not arranged radially in proportion to the mestome-bundles, but in proportion to the cross-section of the stem itself. We notice, therefore, in Lipocarpha that each of the outer mestome-bundles is surrounded by a closed sheath of palisade-cells, all of which contain an abundance of chlorophyll-grains. A similar sheath of palisade-cells is, also, observed on the leptome-side of the inner mestome-bundles, adjoining the arch-shaped group of stereome on the hadrome-The inner mestome-bundles are, hence, surrounded side. partly by palisade-cells and stereome. In no other part of the stem is palisade-parenchyma observable, as the spaces between the outer mestome-bundles are occupied by the several layers of epidermis.

While this singular arrangement of the palisade-cells in the stem of Lipocarpha seems to offer an excellent character by itself, it is, nevertheless, invariably followed by another and still more remarkable feature, represented by the structure of the mestome-bundles. We have already mentioned that the stem possesses two distinct, concentric bands of mestomebundles, an outer and an inner. The majority of the mestomebundles are situated in the peripherical band and represent two forms: small and in transverse section orbicular, and larger which are oval in cross-section. The orbicular are the most abundant, but they do not all possess a leptome and hadrome developed to the same extent as the larger, the oval bundles, nor are they all supported by subepidermal stereome, as these invariably are. Those of the inner band are all large and show a very pronounced oval outline; besides this, they are only supported by stereome on their hadrome-side. But all these inestome-bundles, the large and the small, show the presence of a typical mestome-sheath, the cells of which are but slightly thickened in those species which we have had an opportunity to examine. Inside the mestome-sheath is still another sheath, the cells of which are conspicuously larger than those of the mestome-sheath, very thin-walled and filled with chlorophyll. However the chlorophyll in this sheath differs in a very marked degree from that of the palisade-tissue by not being differen-

\* This Journal, vols. iii, iv, v and vi.

tiated as "grains," and by its more intense green color. This is the sheath which Haberlandt has mentioned as characteristic of *Papyrus cicuta*, and which Rikli has so excellently described after he detected it in other genera of the *Scirpoideæ*. While Duval-Jouve was well aware of the radial arrangement of the palisade cells around the mestome-bundles in several species of *Cyperus*, as his illustrations show, he does not seem to have noticed the inner sheath, the "chlorophyll-sheath," at least he does not figure or mention it.\*

While the chlorophyll-sheath is completely closed in all the peripherical mestome-bundles, which, as stated above, are also surrounded by an uninterrupted sheath of palisade-cells, it merely occurs around the leptome in the mestome bundles of the inner band. We remember from the above that these bundles are not surrounded by palisade-cells excepting on their leptome-side, and it seems as if the development of the inner, "the chlorophyll-sheath," is somewhat depending on the presence of palisade-cells; at least the chlorophyll-sheath is strictly confined to that part of the mestome, which is, also, surrounded by palisade cells. These structural peculiarities: the development of the assimilating tissue into sheaths around the mestome-bundles and accompanied by an inner chlorophyllbearing sheath, does not seem to depend upon any particular mode of growth, if we merely consider the stem. We have noticed this same structure in cylindrical as well as in triangular stems of certain genera of *Cyperacew*, in erect as well as in curved, besides in the singular flattened stems of *Fimbris*tylis autumnalis R. et S. It seems, therefore, hardly probable that the presence of these sheaths depends on any particular

\* Professor Warming (Halofyt-Studier, p. 259) insists that Duval-Jouve, not Haberlandt, should have credit for the discovery of these peculiar sheaths, stating that Duval-Jouve in the year 1875 described and illustrated these as characteristic of a number of *Gramineæ*. However, the chlorophyll-sheath, the one that lies close up to the mestome-sheath and which borders immediately on the leptome and hadrome, has so far never been observed in any of the *Graminææ*. What Duval-Jouve describes and figures is a sheath of palisade-cells, a parenchyma-sheath, that surrounds the mestome-bundles and finally a mestome-sheath, inside of the parenchyma-sheath. But in none of his descriptions or in his illustrations has Duval-Jouve hinted at the existence of a chlorophyll-sheath inside of the mestome-sheath. It is true, that the mestome-bundles in the leaves of several *Graminææ*, for instance *Cymodon*, exhibits three sheaths: one of radially arranged palisade-cells, a second the ordinary parenchyma-sheath, and a thrd the mestome-sheath, but none of these correspond with the sheath which Raberlandt detected inside of the mestome-sheath in certain *Cyperæ*, and which Rikli has lately discussed in his very important paper on this subject. Furthermore Professor Warming states, that although Duval-Jouve did mention and figure the palisade-sheath as characteristic of several French *Cyperus*-species and *Galilea*, he, nevertheless, seemed to have overlooked the inner one "the chlorophyll-sheath" of Rikli.

While the mere question of priority is a very unimportant one in scientific research, it must be admitted that Haberlandt was the first to discover this particular sheath in the Cyperaee.

position of the stems in proportion to the light, and by comparing leaves of various genera no apparent connection seems to exist between their presence and the shape or direction of the leaf-blades. The genus *Fimbristylis*, for instance, on which the writer has prepared an article for this Journal, exhibits a most remarkable variation of growth as regards stem and leaf, yet invariably possessing the same arrangement of the palisade-cells and development of the inner chlorophyll-bearing sheath.

Whether the radial arrangement of the palisade-cells around the mestome-bundles is beneficial to the plant, is a question that cannot be settled at present. It is, also, very uncertain whether the dark, green chlorophyll of the inner sheath possesses a higher assimilating power than that surrounding; very diverse opinions have been expressed regarding these questions, and a brief summary may be found in the work of Warming, cited above.

In returning to the stem-structure of *Lipocarpha*, the leptome and hadrome have attained their highest development in the inner mestome-bundles, but are not, in any of the species we have examined, separated from each other by thick-walled mestome-parenchyma, as described by Rikli (*L. argentea*). There is, furthermore, a large, solid pith which is composed of thin-walled cells, hexagonal in transverse section, in *L. sphacelata* and *L. maculata*; in *L. argentea* and *L. microcephala*, on the other hand, we noticed the pith to be interrupted by large and apparently very irregular lacunes. Cells containing tannin were observed in the pith, close to the mestome-bundles.

Very different is the structure of rhachis, that part of the stem which bears the spikelets. The bark-parenchyma contains no chlorophyll and forms a broad ring around the central-cylinder; the mestome-bundles are mostly small and surrounded by a typical, colorless parenchyma sheath and a thin-walled mestome-sheath, while the inner sheath is totally absent. The arrangement of the mestome-bundles is, also, different, there being a closed band near the center of the axis, while a few are seen to be scattered towards the periphery, entering the rhacheolæ of the spikelets. The rhachis seems totally destitute of stereome and the solid pith occupies only a small part of the central-cylinder. Furthermore we observed that tannin was present in some of the pith-cells as well as in the bark-parenchyma.

### The leaf.

The stem-leaves of the species of *Lipocarpha*, which have been examined, are rather weak, with narrowly linear blades, closed tubular sheaths, but no ligule. The margins of the

blade are mostly involute, and the blade, which is often very asymmetric, is not carinate. The outline of the blade, when considered in transverse section, is broadly crescent shaped in L. maculata with the two halves of unequal size (fig. 3). The same is, also, the case with L. argentea, but the blade is, in this species, constricted above the midrib and is thinner in proportion to its width than in the foregoing species (fig. 4).  $\mathbf{The}$ blades of *L. microcephala* and *L. sphacelata* are less asymmetric and equally thin throughout. The epidermis of the lower surface of the leaf-blade shows the same development as in the stem with a single layer outside the mestome-bundles and two or three rows of cells between these. But on the upper face of the blade in L. argentea and L. maculata we find a huge mass of epidermal tissue in layers of considerable width, from five to six, especially towards the margin; in L. microcephala and L. sphacelata, on the other hand, there is but



FIG. 3. Leaf of L. maculata, transverse section.  $\times$  60.



FIG. 4. Part of leaf of L. argentea, transverse section.  $\times 60$ .

one single layer on either face of the blade. In considering L. maculata and L. argentea the outer layer of epidermis consists of much smaller cells than the inner ones, especially towards the margins, where two or three subepidermal stereomebundles are located. While the outer epidermis in L. argentea is developed as bulliform cells above the midrib (fig. 4), where no inner layers are developed, we notice in L. maculata, on the same place, a tendency of the outer epidermis to develop in the same way, as bulliform cells, but are separated from the mesophyll by at least two layers of inner epidermis. In the

two other species the epidermis of the upper face consists of a single laver of cells of almost equal size, but does not seem to develop as groups of bulliform cells, so commonly observed in other genera. The epidermis of the lower surface of the leaf is composed of cells of nearly equal width excepting those which cover the stereome; these are usually much smaller and contain cones of silica. While the lower surface is very even in L. maculata and L. argentea, we noticed in the two other species distinct furrows between the stereome-bundles like those described above as characteristic of the stem. The stomata are located at the bottom of these furrows, while in L. argentea and L. maculata they are freely exposed, being on a level with the surrounding epidermis. As regards the mesophyll, this is developed as a sheath around each mestomebundle, separating these from the stereome of the leptome-side. Thus there exists a strong analogy in structure when we compare the bark of the stem with the mesophyll of the leaf. besides this the mestome-bundles in both show an absolutely identical composition. The mestome- and chlorophyll-sheath are developed to the same degree we noticed in the stem, and the mestome-bundles are, also, here represented by two forms: orbicular and oval, when considered in transverse sections (fig. 5).



Stereome is developed outside the larger mestomebundles on the lower surface of the blade, but occurs, also, in one or two isolated groups on the upper face and close to the margin. The margin itself merely consists of the two layers of epidermis with no support of stereomatic tissue.

### The bracts,

FIG. 5. Leaf of *L. maculata*, showing an orbicular mestome-bundle with its three sheaths; tannin in a cell drawn with black;  $E_{P.} = \text{epidermis}$  of lower surface.  $\times 400$ .

which subtend the spikelets, are membranaceous and contain only one mestome-bundle, located in the middle and forming a slightly projecting

rib on the dorsal face. There is an epidermis of large and thin-walled cells on both faces of the bract, with the exception of the margins, where only one stratum of epidermis is developed. A few of the cells contain tannin, but no chlorophyll. The mestome-bundle is surrounded by a single sheath, a mestome-sheath, the cell-walls of which are but very slightly thickened. Stereome is present and forms isolated bundles on the lower surface, one near the midrib, and two on each side, a short distance from the margins.

### The prophyllon

of the spikelet shows a very simple structure, there being no mestome but merely about five ribs of stereome, two of which are larger than the others so as to render the leaf bicarinate. Epidermis is developed on both faces excepting near the margins, where it becomes reduced to one single layer. The epidermal cells are very thin-walled, and none are developed as bulliform cells.

### The bract

of the flower shows nearly the same structure as that of the spikelet, but much thinner (fig. 6). The epidermis is reduced



FIG 6. Transverse section of a floral bract of L. maculata, showing the midrib and half of the blade; cells containing tannin are drawn with black.  $\times 320$ .

to a single layer in the lateral parts, from the midrib to the margins, while the margins themselves possess a double epidermis. Stereome is present, but only on the dorsal face of the scale covered by epidermis, and tannin-reservoirs were observed in some of the epidermal cells, indicated with black in the accompanying figure (fig. 6).

### The pericarp

consists of three distinct layers: an outer epidermis of very thin-walled cells, each containing a silicious cone with minute



FIG. 7. Transverse section of the pericarp of *L. maculata.* Ep = the outer epidermis; Scl. = the layers of sclereids; ep. = the inner epidermis.  $\times$  560.

warty surface, a few strata of sclereids, and finally an inner epidermis. The cells of the inner epidermis are very thin-walled and show a rectangular outline in transverse sections (fig. 7). A skeleton of silica is readily obtained by the usual preparation, and shows that not only the cones are silicified, but also a part of the epidermis above these (figs. 8 and 9).

The roots are very slender and show a rather open structure.

There is a thin-walled hypoderm underneath the epidermis, and the bark is traversed by lacunes of considerable width. The endodermis has the cell-walls thickened all around, representing an O-endodermis, inside of which is a pericambium interrupted by proto-hadrome. The innermost part of the root is occupied by a thick-walled conjunctive tissue with a single or sometimes two large vessels in the center.





FIG. 8. Epidermis of pericarp of L. maculata, seen from above, showing the silica-skeleton.  $\times 560$ .

FIG. 9. Same as figure 8, but seen from the side.  $\times$  560.

In considering the anatomical structure of these four species of *Lipocarpha*, it seems that our genus possesses several characters by which it may be distinguished from a number of the other genera, studied so far. The species themselves, may, also, be recognized in this way, their anatomical characters being as follows:

The leaf.	Outer cell-walls of epidermis	Outer cell-walls of epidermis rougly thickened.	Outer cell-walls of epidermis toderately thickened.	Subepidermal stereome in fur- ows.	Subepidermal stereome form	Bulltform cells above midrib.	No builitorm cells.	Epidermis of several layers on pper face.	Epidermis of a single layer on pper face.
L. maculata	_		+	+	_	_	+	+	
L. argentea		+	-	+	-	+	_	+	_
L. sphacelata	-		+	+	_	-	+	-	+
L. microcephala	+	_	_	_	+	_	+	_	+

If we finally compare these anatomical characters with those which Rikli observed in L. argentea, we will notice a few divergencies. This author states, for instance, that the leaf possesses one mediane and numerous lateral groups of bulliform cells, while the leaves we examined showed only one, above the midrib (fig. 4); besides that the lateral parts of the blade were covered by several layers of large-celled epidermis. Furthermore is stated that the leptome and hadrome are separated from each other by a zone of thick-walled cells (mestome-parenchyma), which we did not notice in any of the species examined. It seems as if the leaf, which Rikli described, may not have belonged to L. argentea, and perhaps not to Lipocarpha at all. It is, also, to be pointed out that not all of the Cyperaceæ, in which a chlorophyll-sheath is developed, have a scarcity of stereome, since this tissue is well represented in the species of *Lipocarpha*.

Brookland, D. C., October, 1898.

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### ART. XVIII.—The Granitic Breccias of Grizzly Peak, Colorado; by George H. STONE.

GRIZZLY PEAK is situated about twenty-three miles southwest of Leadville, and forms the watershed from which streams flow northwest into the Roaring Fork and the Grand, southwest into the Gunnison, and east into the Arkansas. Its elevation is marked by Hayden as 13,956 feet. It is the highest pinnacle of a very irregular volcanic mass consisting of several radiating ridges one to five miles long.

The eruptive rocks of the district are marked on Hayden's Atlas of Colorado as rhyolite. They contain a large amount of uncombined silica, but sanidine is not abundant, and they more nearly resemble the quartz porphyries of Leadville than the ordinary sanidine-bearing rhyolites of central Colorado. Dark silicates occur only in small quantities locally. The volcanic mass is situated in the midst of a region of schists containing dikes and irregular bodies of granite.

The volcanic ridges have steep lateral slopes. Cliffs abound, though in many places the rock disintegrates so as to form a smooth talus of small fragments. There are a few somewhat symmetrical cones, but the general outline of the ridges is rugged, and their tops form a sierra. In several places large areas are colored bright red, and the local name for the central mass where Grizzly Peak is situated, is Red Mountain. The color is due more to the oxidation of pyrite than to the decomposition of iron-bearing silicates.

Wherever the lava is exposed on the surface, as it often is toward the tops of the ridges and on some projecting bosses and crags, it is somewhat scoriaceous and decomposed. But over most of the higher portions of the ridges the lava is capped by a layer of breccia composed mostly of fragments of the lava that are only a little polished and rounded at the angles. In some places are many subangular fragments of granite or schists lying upon or among the lava fragments, often being so abundant as to form all of the surface layer of the breccia near the top of the mountains. I saw a granite bowlder six feet in diameter embedded in a solid breccia consisting of lava fragments.

In some cases the volcanic rock extends to near the bottoms of the ridges, but in general it forms the upper half or twothirds of the ridges. Over the lower portions of the volcanic ridges and thence extending for a short distance down the slopes over the adjacent granite and schists, we find a superficial layer of firmly cemented breceia consisting wholly of rather

### G. H. Stone-Granitic Breccias of Colorado.

small fragments of schists with some granite. In several places this is shown by mining tunnels to be fifty and sometimes even more than one hundred feet thick. I found one tunnel that had penetrated the breccia into granite and schists in place, in the midst of which is a vertical dike of quartz porphyry bordered on each side by a vertical layer of breccia several feet in thickness. This was composed almost if not entirely of crushed granite and schists. In places the granitic breccia forms a terrace along the side of the mountain. Ι noticed one place where this breccia rests on schists that have been broken, faulted, and brecciated along the lines of fracture, so that blocks of schistose rocks twenty to sixty feet in diameter are separated by zones or vein-like bodies of schist-breccia one to four feet thick. The fragments are only a little rounded. although different kinds of schists are promiscuously mixed, showing that there was considerable faulting.

In a paper on the "Granitic Breccias of the Cripple Creek District" " I have described somewhat similar breccias to those found in the Grizzly Peak district, but on a far larger scale than the latter. However, the latter are very suggestive when we study the question of origin.

Obviously when ejectamenta were hurled by violent explosions over a large area adjacent to the volcanic vents, to form substantially horizontally-bedded breccias or conglomerates, as was the case in the San Juan mountains, Colorado, and in the Sierra Blanca range, Lincoln County, New Mexico, the fragments of the older rocks that were ejected from the vents ought to have been covered and mixed with later ejectamenta composed of volcanic rocks. But in the case of the dikes at Cripple Creek above cited, also those at Grizzly Peak, we find the fragments of older rocks overlying the fragments of volcanic rocks, and these in turn overlying rather narrow dikes that show but little lateral flow of the lava. The interpretation is plain. These dikes rose quietly and slowly through the pre-existing rocks. Before reaching the surface they became sufficiently solid at their upper extremities to be able to push fragments of the older rocks before them. In some cases the latter were at once cemented fast to the tops of the rising dikes or to the fragments of volcanic rock that were formed by the breaking up of the thin crust of solidified lava, as the dike slowly but irresistibly rose above the pre-existing surface. In such cases they were cemented fast to the rising dike before they could be washed away. In other cases, as the dikes rose above the original surface, the fragments of granite, schists, or other rocks penetrated by the dikes, remained for a time uncemented. Under the action of gravity, frost, rain-wash, etc.,

\* This Journal, vol. v, Jan., 1898.

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most of these loose fragments then slid down from the tops of the rising dikes and formed a talus over the lower slopes of the dikes and thence for a short distance over the adjoining country rocks. Here they were subsequently cemented into firm breccias.

I see no possible way for explosive volcanic eruptions to preserve large masses of fragments of the older rocks free from mixture with fragments of lava, and still less to leave them overlying all other volcanic matter.

Bowlders of the so-called rhyolite of the Grizzly Peak district are found in the moraines at Twin Lakes. This proves that the volcanic eruption occurred before the glacial epoch. The position and mode of deposition of the granitic breecias prove that at the time of the eruption the Sawatch range was already deeply dissected by erosion, and that there has not been very much erosion since.

In the paper above cited I have described the gold-bearing granitic sand-rock that formed out of the granite crushed by a rising phonolite dike at the Alhambra mine, Cripple Creek district. The facts there described show that vein waters, probably waters heated by the dike which still remained in a molten condition a few feet below the solidified upper crust, decomposed the grains of crushed granite, honeycombing the sand and replacing much of the feldspar with silica and finally cementing the sand into a firm rock. The mineralized surface crust of sand-rock was in places charged with many times as much gold as is contained in any vein that has been found below in the granite or in the phonolite dike.

Any complete theory of vein deposits will have to treat of the mineralization of the superficial crusts of breccia that formed above and along the margins of rising dikes. There are numerous instances of this class of superficial ore deposits found among the granitic breccias of the Grizzly Peak region, but the subject requires more detailed treatment than is possible within the present paper.

Colorado Springs.

### ART. XIX.—The Constitution of the Ammonium Magnesium Phosphate of Analysis; by F. A. GOOCH and MARTHA AUSTIN.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXIX.]

In a recent paper from this laboratory<sup>\*</sup> it has been shown that the presence of ammonium chloride or other ammonium salt is necessary in the precipitation of manganese as the animonium manganese phosphate by microcosmic salt in order that the precipitate may have the ideal constitution represented by the symbol NH<sub>4</sub>MnPO<sub>4</sub>.

It was also shown that the solvent effect of the ammonium chloride upon the precipitated ammonium manganese phosphate is not marked when an excess of the precipitant is present in solution.

The relations disclosed in this paper suggest that the chemical constitution of the precipitate rather than mechanical contamination and varying solubility—the explanations generally accepted, and, indeed, advocated by one of us in a former paper†—may be responsible for observed variations in the weight of the residue derived by the ignition of the similar salt of magnesium, the ammonium magnesium phosphate, precipitated by an excess of a soluble phosphate from the solution of a magnesium salt, or from the solution of a soluble phosphate by an excess of a magnesium salt.

### Precipitation by Excess of the Soluble Phosphate.

The precipitation of the magnesium salt by an excess of the soluble phosphate was first studied. For this work a solution of pure magnesium nitrate was prepared by dissolving the pure magnesium oxide of commerce in a slight excess of pure hydrochloric acid and boiling with more magnesium oxide. After filtering off the excess of magnesium oxide and any trace of iron or members of the higher groups, the solution was precipitated by ammonium carbonate, the precipitate was washed by repeated boilings and filtrations until silver nitrate gave no precipitate in the solution acidified with nitric acid. This precipitated carbonate was nearly dissolved in nitric acid and the solution was boiled with an excess of the carbonate (for the purpose of removing traces of barium, strontium, and calcium) filtered, and diluted to definite volume. The evaporation of a definite volume of the solution and strong ignition of the residue would be a most natural method of establishing a standard

> \* This Journal, vi, 233. † Am. Chem. Jour., i, 391.

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of the solution, were it not for the fact pointed out by Richards and Rogers\* that the oxide of magnesium retains on ignition occluded nitrogen and oxygen enough to increase its weight sensibly. For this reason the nitrate was converted to the sulphate and weighed as such-either by evaporating to dryness in a weighed platinum crucible a definite volume of the solution, igniting as oxide, and changing to the sulphate by heating with sulphuric acid; or, by evaporating the magnesium nitrate directly with an excess of sulphuric acid of half strength. In this treatment the excess of acid was removed by heating the platinum crucible upon a porcelain ring or triangle so placed within a porcelain crucible that the bottom and walls of the inner crucible were distant about one centimeter from the bottom and walls of the outer crucible. The excess of acid is easily removed in this way, and the outer crucible may be heated to redness without danger of breaking up the magnesium sulphate. The results of this work, taking  $\dot{O} = 16$ ,  $\dot{M}g = 24.3$ ,  $\dot{N} = 14.03$ , S = 32.06, are given in the accompanying table.

	TABLE I.	
MgSO <sub>4</sub> obtained by converting ignited MgO into the sulphate.	MgSO <sub>4</sub> obtained directly from 50° <sup>m3</sup> Mg(NO <sub>3</sub> ) <sub>2</sub> .	Theoretical amount of MgO in MgSO <sub>4</sub> .
grm.	grm.	grm.
0.5748		0.1924
0.5739		0.1923
	0.5741	0.1922
	0.5750	0.1925

The magnesium oxide obtained by direct ignition of the nitrate weighed on the average about 0.0010 grm. more than the oxide theoretically present in the weighed sulphate from equal portions of the solution.

<sup>1</sup>Before proceeding to study possible chemical effects of ammonium chloride in determining the constitution of the ammonium magnesium phosphate, it is obviously necessary to define the extent to which the ammonium salt may exert a solvent action in presence of the precipitant. Fresenius estimated that ammonium magnesium phosphate is soluble in 15293 parts of cold water, but the method of investigation employed did not entirely preclude the possibility of counting as ammonium magnesium phosphate soluble material included and held in the original precipitate.<sup>†</sup> According to Kissel<sup>‡</sup> the phosphate, which dissolves in a mixture of ammonia and water in the proportion of 0.0040 grams to the liter and in the proportion of 0.0110 grams to the liter in a similar mixture

\* Am. Chem. Jour., xvi, 567.

+ Fresenius, 6te Aufl., p. 805.

‡ Zeitschr. für Analyt. Chemie, viii, 173.

containing also eighteen grams of ammonium chloride, is practically insoluble in the latter mixture if an excess of magnesia mixture be added; and Heintz \* showed that the effect of adding an excess of sodium phosphate in the solution is similar.

So far as appears, no quantitative experiments have been recorded in which the behavior of a mixture of ammonium chloride and magnesium salt and an insoluble phosphate in a solution only slightly ammoniacal has been tested, though as a matter of convenience the use of faintly ammoniacal solutions and faintly ammoniacal washwater is to be preferred to the mixture of strong ammonia and water [1:3] ordinarily employed. As a preliminary step, therefore, in the work to be described, experiments were made to find how small an amount of magnesium could be detected in solution by precipitating with microcosmic salt, either alone or in presence of ammonium chloride in faintly ammoniacal solutions. The ammonium chloride used for these tests (as well as in the similar quantitative work following) was purified by boiling with a faint excess of ammonia, filtering, digesting twelve hours with microcosmic salt, and filtering again. The results are given in Table II.

000		***
	DIT	
1 4	DLL	
_	_	_

MgO taken as	H(NH <sub>4</sub> )NaPO <sub>4</sub> .			
the nitrate.	4H2O taken.	Volume.	NH₄Cl taken	Opalescent
grm.	grm.	$\mathrm{cm}^3$	grm.	precipitation.
( 0.0003	1.75	100		marked
10.0003	<b>66</b>	500		66
( 0.0003	<b>6</b> 6	100	10	66
\$ 0.0003	"	500	10	66
0.0003	"	500	30	faint
0.0001	66	100		marked
( 0.0001	"	100	10	66
{ 0.0001	66	500	10	faint
( 0.0001	"	500	60	"

The results of these tests show that even so little as 0.0001 grm. of magnesium oxide may be detected in five hundred cubic centimeters of faintly ammoniacal water containing as much as sixty grams of ammonium chloride.<sup>+</sup> It is plain that strongly ammoniacal liquids are entirely unnecessary in the precipitation of the ammonium magnesium phosphate under

\* Zeitschr. für Analyt. Chemie, ix, 16.

Weight of

<sup>†</sup> It was found also, incidentally, that the presence of reasonable amounts of ammonium oxalate (100 <sup>cm3</sup> of the saturated solution) does not interfere with the precipitation of the ammonium magnesium phosphate by microcosmic salt. the conditions. In nearly all the experiments to be detailed use was made, therefore, of faintly ammoniacal solutions and wash-water.

In Table III are given the results obtained in a study of the effects of varying proportions of ammonium chloride and the soluble phosphate upon the constitution of the precipitate. All precipitates were gathered upon asbestos in the filtering crucible, washed in faintly ammoniacal water, and ignited as usual. In every case the precipitation was practically complete; for, upon allowing the filtrates with the wash-water to stand for several days after further addition of microcosmic salt, nothing but insignificant traces of a precipitate --- not exceeding 0.0001 grm. - ever appeared. In the experiments of section A precipitations were made in the cold by the action of microcosmic salt in considerable excess upon the solutions of magnesium nitrate containing varying amounts of ammonium chloride. In experiments (1) to (5) the liquid was made faintly ammoniacal after the addition of the precipitant and the precipitate was filtered off immediately after complete subsidence; in experiments (6) to (10) the precipitate first thrown down was redissolved in a very little hydrochloric acid and reprecipitated by dilute ammonia (the operation being repeated several times) with a view to improving the crystalline condition of the precipitate, and this treatment introduced. of course, a small amount of ammonium chloride, probably less than a gram. It will be observed that errors of excess appear in all of these determinations, those being the greatest in the experiments in which the largest amounts of the ammonium salt were present.

In the experiments of section B the manipulation was so changed that the supernatant liquid was poured off (through the filtering crucible which was to be used subsequently to collect the phosphate) after the precipitate had subsided and the insoluble phosphate was dissolved in hydrochloric acid and brought down again, after dilution, by the addition of a faint excess of dilute ammonia. By thus removing the supernatant liquid after the first precipitation, the excess of the precipitant and the amounts of ammonium chloride originally present were reduced to relatively low limits, so that their effects in the reprecipitation were at a minimum; and by adding varying amounts of ammonium chloride, or none at all, before the reprecipitation, it became possible to demonstrate the individual effect of that reagent apart from that of an excess of the microcosmic salt. It will be noted that in experiments (11) and (12), in which no ammonium salt was added after the decantation from the first precipitate, the results are ideal, and that the errors of excess advance as the amounts of ammonium
salt present in the final precipitation increase. The quantity of the ammonium salt present during the first precipitation does not influence the error in the final precipitation unless it is so large that a simple decantation of the supernatant liquid would naturally leave an appreciable amount of it to act when the second precipitation takes place.

				LAB	LE LLL.			
		$Mg_2P_2O_7$						
	cor	responding		Error in	Error in		HNaNH <sub>4</sub> P	04.
	to	Mg(NO <sub>3</sub> ) <sub>2</sub>	$Mg_2P_2O_7$	terms of	terms of	NH4Cl	4H <sub>2</sub> 0	
		taken.	found.	$Mg_2P_2O_7$ .	MgO.	present.	used.	Volume.
		grm.	grm.	grm.	grm.	grm.	grm.	$\mathrm{cm}^{3}$ .
		U	0	A		9	0	
(	1)	0.5311	0.5418	+0.0102	+0.0038		2.5	150
ì	2)	0.5311	0.5462	+0.0121	+0.0057	2	"	150
ì	3)	0.5311	0.5408	+0.0091	+0.0035	2	"	150
ì	4)	0.5311	0.5500	+0.0189	+0.0068	60	6.6	250
Ì	5)	0.2311	0.5520	+0.0209	+0.0075	60	6.6	250
`	í.							
(	6)	$0\ 5311$	0.5345	+0.0034	+0.0015	*	66	150
(	7)	0.2311	0.5371	+0.0060	+0.0025	*	"	150
(	8)	0.2311	0.5384	+0.0013	+0.0026	*	41	150
(	9)	0.2311	0.5386	+0.0012	+0.0021	*	66	150
(	10)	0.2311	0.5412	+0.0104	+0.0031	*	"	150
				В	5			
,		0.5911	0.7210	. 0.0001		*		150100
٢	11)	0.5311	0.5312	+ 0.0001	+ 0.0000	~ <u></u>		150,100
ļ	12)	0.5311	0.5311	+ 0.0000	+0.0000			150,100
ì	13)	0.5311	0.5346	+0.0032	+0.0013	2 + 2		150,100
1	14)	0.5311	0.5348	+0.0031	+0.0014	2 + 2		150,100
(	10)	0.2311	0.2383	+0.0015	$\pm 0.0056$	5 + 5		150,100
ļ	16)	0.2311	0.2368	+0.0057	+0.0021	5 + 5		150,100
(	17)	0.2311	0.5376	+0.0065	+0.0023	10 + 10		200,100
(	18)	0.2311	0.5395	+0.0084	+0.0030	10 + 10		200,100
(	19)	0.2311	0.2396	+0.0082	+0.0031	60 + 5		250,100
(	20)	0.2311	0.2389	+0.0018	+0.0058	60 + 5		250,100

It is plain that the errors of excess which appear when either the ammonium chloride or the soluble phosphate is present in considerable amount, must be due either to mechanical inclusion on the part of the highly crystalline precipitate, or to variation in the ammonium magnesium phosphate from the ideal constitution toward a condition represented by a phosphate richer in ammonia and correspondingly deficient in magnesium. If any appreciable amount of the ammonium chloride present were held by the precipitate, it would naturally be represented by magnesium chloride after ignition, but, in no one of these experiments, even in those dealing with sixty grams of ammonium chloride, did the residue, after dissolving in nitric acid, give with silver nitrate evidence of the presence of more than a mere unweighable trace of chloride. A special experiment, moreover, in which an attempt was

\* Probably less than 1 grm

made to determine the silver chloride precipitated from the solution in nitric acid of an unignited precipitate thrown down by microcosmic salt in presence of sixty grams of ammonium chloride, confirms this conclusion : the precipitate was unweighable. If ammonium chloride present in the solution to so great an amount is not included in the precipitate in significant quantity, it would seem to be unnatural that the microcosmic salt should be included mechanically in any very great amount. But unless the microcosmic salt was mechanically included, the increase in weight must be due to the chemical influence of the reagents-that is, to the production of a phosphate rich in ammonium and deficient in magnesium. Ber zelius\* recognized the existence of such a phosphate of magnesium; but Wach, in following the work of Berzelius, failed to find it. No attention seems to have been given since to the existence of such a salt. It would be natural to expect its formation, if ever, when the precipitating phosphate is in excess and ammonium salts are present in abundance, with free ammonia. Obviously the natural effects of all these reagents would be toward the production of a salt holding more ammonia and more phosphoric pentoxide for a given amount of magnesium. The results of the table seem to point strongly to such tendencies, and, by inference, toward the existence of such a compound. Thus in experiments (11) and (12), in which the greater part of this excess of microcosmic salt was removed by decantation before the second precipitation, while no ammonium chloride was present excepting the small amount made by the solution and reprecipitation of the first precipitate, the error is practically nothing. In experiments (13) and (14), (15) and (16), (17) and (18), all similar to (11) and (12) excepting that ammonium chloride was present, the average errors— +0.0036 grm. in terms of magnesium phosphate, 0.0064 grm., +0.0074, respectively—increase as the ammonium chloride is increased in the final precipitation. In experiments (19) and (20), in which the ammonium chloride amounted to sixty grams in the first precipitation and to five grams in the second in addition to the amount that would naturally remain after decanting the strong solution of the former precipitation, the similarity of this error (+0.0082 in the mean) to that of the experiments in which smaller amounts of the ammonium chloride were used throughout goes to show that only the amount of ammonium salt present in the final precipitation counts. Further, a comparison of corresponding experiments of A and B shows very plainly that the treatment which involves the removal of the large part of the micro-

\* Berzelius, Jahresbericht 3 Jahrgang (1824) übersetzt von C. G. Gmelin s. 92. † Schweigger, 1830, Band 29, s. 265. cosmic salt, the solution of the precipitate, and reprecipitation tends to reduce the higher indications. Thus, for example, the error in (2) and (3) is +0.0124 grams in terms of magnesium pyrophosphate, while in (13) and (14), similarly carried out except the decantation of the excess of the precipitant, solution and reprecipitation, the error is +0.0036 grm.

The special influence of free ammonia during precipitation, was investigated in the following experiments. Definite volumes of the magnesium nitrate solution were drawn from a burette into a platinum dish, ammonium chloride-10 grm.was added, the magnesium was brought down by dilute ammonia in presence of microcosmic salt, and strong ammonia equal to one-third the volume of the solution was added. The solutions, after standing, were filtered off on asbestos under pressure in a perforated crucible, and the precipitates were washed with ammonia diluted to the proportion of three parts of water to one of ammonia, dried after moistening with a drop of saturated solution of ammonium nitrate, ignited and weighed. The results are given in experiments (1) and (2) of Table IV. In these determinations the mean error reaches +0.0183 grm. in terms of magnesium pyrophosphate; while in experiments (3) and (4), made similarly excepting that the supernatant liquid was decanted from the precipitate first thrown down, the precipitate dissolved in hydrochloric acid, and after dilution reprecipitated by dilute ammonia immediately supplemented by enough strong ammonia to make onefourth the volume of the entire solution, the error amounts in the mean to +0.0061 in terms of the pyrophosphate.

	$Mg_2P_2O_7$						
corresponding			Error in	Error		HNaNH <sub>4</sub> P	04.
to	$Mg(NO_3)_2$	$Mg_2P_2O_7$	terms of	in terms	$NH_4Cl$	$4 H_2 O$	
	taken.	found.	$Mg_{2}P_{2}O_{7}$ .	of MgO.	present.	used.	Volume.
	grm.	grm.	grm.	grm.	grm.	grm.	$cm^3$ .
(1)	0.5311	0.5503	+0.0195	+0.0069	10.	2.5	200
(2)	0.5311	0.5505	+0.0194	+0.0010	10	2.5	200
					$\sim$		
(3)	0.2311	0.2393	+0.0085	+0.0029	10,	2.5	200,100
(4)	0.5311	0.5351	+0.0040	+0.0011	10, -	2.5	200,100

TABLE IV.

In experiments (1) and (2) the precipitate was influenced by an excess of microcosmic salt, ammonium chloride, and free ammonia in large amount; in experiments (3) and (4), by decanting in the manner previously described, by dissolving the precipitate, and reprecipitating, the effects of an excess of microcosmic salt and ammonium chloride are reduced to a minimum, and, in a comparison of the results with those of experiments (11) and (12) of Table III the tendency of the free

ammonia comes to view. The results discussed seem certainly to point to a general tendency on the part of free ammonia, ammonium chloride and excess of the phosphate to produce a salt rich in ammonia and deficient in magnesium, which for a definite amount of magnesia precipitated must leave upon ignition a residue weighing more than the normal phosphate.

If it be assumed that a salt of the symbol  $(NH_4)_4Mg(PO_4)_2$ the next natural step to the normal salt, NH, MgPO, - is present in the precipitate, the residue which such a salt would leave upon ignition would be the metaphosphate Mg(PO<sub>2</sub>). From the relations of the symbols for magnesium pyrophosphate and magnesium metaphosphate the weight of the residue obtained, and the weight of the pyrophosphate theoretically derivable from the weight of magnesium salt used, it is possible, of course, to calculate the proportionate amounts of pyrophosphate and metaphosphate present in any ignited residue. Proceeding in this manner, it appears, that, in order to account for the variations noted, it is necessary to assume the presence in many cases of very considerable amounts of the metaphosphate. Thus, in the case of those results obtained according to the usually accepted method of precipitating and washing with strongly ammoniacal liquids, viz. in experiments (1) and (2) of Table IV, the proportion of metaphosphate needed to account for the observed error reaches ten per cent.

## Precipitation by Excess of the Magnesium Salt.

The relations which obtain in the reverse process of precipitation-the action of an excess of the magnesium salt upon a soluble phosphate-were studied in experiments to be described. A solution of pure hydrogen disodium phosphate was prepared by carefully recrystallizing the pure salt of commerce five times from distilled water in a platinum dish, dissolving the crystals, and diluting to definite volume. The standard of the solution was established by evaporating to dryness in a weighed platinum crucible known volumes of the solution, igniting the residue and weighing the sodium pyrophosphate. Magnesia mixture, the precipitant, was prepared by dissolving fifty-five grams of magnesium chloride in as little water as possible and filtering, mixing with this solution twenty-eight grams of ammonium chloride purified by treating it in strong solutior with bromine water and a slight excess of ammonia, filtering, diluting to one liter, and, after standing for some hours, filtering again.

The tests of the following table show that the precipitation of a soluble phosphate by the magnesia mixture is practically complete in faintly ammoniacal solutions even when very dilute and charged with large amounts of ammonium chloride, provided the magnesia mixture is present in sufficiently large excess. TABLE  $\nabla$ .

$P_2O_5$ in				
$HNa_2PO_4$	Magnesia			
taken.	mixture.	Volume.	NH₄Cl.	
grm.	$\mathrm{cm}^{3}$ .	$\mathrm{cm}^{3}$ .	grm.	Precipitation.
0.0002	10	100		Visible at once
0.0002	50	100		throughout the liquid.
0.0002	10	100	10	cc -
0.0002	10	200	60	66
0.0001	50	250	60	66
0.0001	10	100		66
0.0001	10	100	10	66
0.0001	50	200	10	66
0.0001	10	250	60	66
0.0001	50	300	60	Visible after
0.0001	50	500	60	settling out.

This conclusion was further substantiated by an actual test (by the molybdate method) of the ignited residue, obtained by evaporating a filtrate from ammonium magnesium phosphate. (equivalent to 0.8614 grams of the pyrophosphate) precipitated by a faintly ammoniacal solution of magnesia mixture in presence of sixty grams of ammonium chloride, which gave a precipitate of ammonium phosphomolybdate yielding 0.0002 grams of magnesium pyrophosphate. It is evident, therefore, that any considerable deficiencies of weight of the magnesium phosphate obtained by precipitating equal amounts of a soluble phosphate by magnesia mixture in presence of varying amounts of ammonium chloride, cannot be attributed to varying solubility of the magnesium phosphate under changing proportions of the ammonium chloride.

The results recorded in section A of Table VI were obtained by treating definite volumes of the pure solution of hydrogen disodium phosphate with magnesia mixture, in slight excess above the amount required to bring down the phosphate, and making the solution distinctly ammoniacal. After thorough subsidence, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed in water faintly ammoniacal, dried, ignited and weighed. In experiments (1), (5) and (6), only the ammonium chloride present in the magnesia mixture was used; in the other cases weighed portions were added. In the experiments of section B, the precipitate was dissolved in hydrochloric acid after filtering off the supernatant liquid, brought down again in dilute solution by ammonia in distinct excess, and thereafter treated as in the experiments of section A. The experiments of section C were conducted similarly to (1), (5) and (6) of A excepting that the magnesium mixture was introduced into the ammoniacal solution of the phosphate drop by drop from a burette. The precipitations in A, B and C were proved to be practically complete; for by treatment of the filtrates with more magnesia mixture and standing, no more than a trace—0.0001 grm. at the most—of the phosphate was found. The ignited residues never contained more than a mere trace of chlorine.

TABLE VI.

Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>		Error			NH₄C	1	Macu
ing to		in terms	Error in		nesia	-	6H.O in
HNa PO	Mg.P.O.	of	terms of		mix.	NH.CI	magnesia
taken.	found.	$Mg_2P_2O_7$	P.	Volume.	ture.	added.	mixture.
grm.	grm.	grm.	grm.	cm <sup>3</sup> .	grm.	grm.	grm.
			A		-	Ŭ	Ū
(1) 0.8615	0.8613	-0.0005	-0.00005	150	1.68		3.3
(2) 0.8615	0.8612	0.0000	0.00000	200	66	20	46
(3) 0.8615	0.8605	-0.0013	-0.00036	200	66	20	44
( 4) 0.8615	0.8561	-0.0024	-0.00121	300	**	60	46
(5) 0.0852	0.0862	+0.0010	+0.00028	100	0.28		0.55
( 6) 0.0852	0.0866	+0.0014	+0.00039	100	66		66
(7) 0.0852	0.0847	-0.0002	-0.00014	200	46	20	66
(8) 0.0852	0.0830	-0.0025	-0.00065	200	44	20	66
( 9) 0·0852	0.0811	-0.0041	-0.00112	300	**	60	**
			в				
(10) 0.8111	0.8114	+0.0003	+0.00008	150,100	1.68	1	3.3
(11) 0.8615	0.8613	-0.0005	-0.00006	150,100	46		"
(12) 0.8615	0.8518	-0.0031	-0.00103	200,100	66		66
(13) 0.8615	0.8487	-0.0158	-0.00328	200,100	66	,60	66
(14) 0.0852	0.0857	+0.0003	+0.00008	100,100	0.58		0,22
(15) 0.0852	0.0626	+0.0004	+0.00011	100,100	**	10,	"
(16) 0.0852	0.0823	+0.0001	+0.00003	150,100	66	10,10	66
(17) 0.0852	0.0819	-0.0033	-0.00095	200,100	"	20,20	
			С				
(18) 0.8111	0.8071	-0.0040	-0.00112	120	1.4		2.75
(19) 0.8111	0.8052	-0.0029	-0.00162	120	1.4		2.75

While the results are not entirely regular, the tendency of the ammonium salt to produce errors of deficiency in proportion to its amount is plain if we compare among themselves the experiments of A upon similar amounts of phosphate, and then those of B upon similar amounts of phosphate among themselves; and by a comparison of corresponding results in A and B it is clearly shown that the presence of an excess of magnesia mixture tends to counteract more or less completely errors of deficiency due to the action of the ammonium chloride. These facts are quite in harmony with the hypothesis that the ammonium salt tends to produce an ammonium magnesium phosphate richer in ammonia and phosphoric acid and poorer in magnesia than the normal salt NH<sub>4</sub>MgPO<sub>4</sub>; for,

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though the production of such a salt in presence of an excess of the soluble phosphate compels the combination of a definite amount of magnesium with more than the normal amounts of phosphoric acid and ammonia (as was the case in the former series of experiments), when the supply of the soluble phos-phate is limited the amount of magnesium associated with it must fall below the normal (as is the case in the present series of experiments). Moreover, the behavior of the precipitant is quite in accord with the hypothesis; for, though the influence of an excess of the soluble phosphate would naturally tend (as was observed) in the same direction as that of the ammonium salt and free ammonia, viz., to the production of the phosphate deficient in magnesium, the tendency of an excess of the magnesium salt must obviously be to increase the amount of magnesium in the phosphate, as was observed in the experi-ments of Table VI. The hypothesis fits the facts, therefore, on both sides; and, if precipitation is practically complete (as was shown to be the case throughout) the argument for the existence of an ammonium magnesium phosphate-poorer than the normal salt in magnesium—possibly the salt (NH4), Mg(PO4), -seems to be strong.

## The Practical Determination of Magnesium and Phosphoric Acid.

In determining magnesium by the procedure in ordinary use, the tendency is strong—as is shown in experiments (1) and (2) of Table IV—toward high plus errors, and the error is due to the combined effects of excesses of the precipitant, the ammonium salt, and free ammonia. The experiments (11) and (12) of B, Table III, show conclusively that such tendencies to error may be counteracted effectively by pouring off the supernatant liquid (through the filter to be used subsequently to collect the precipitate) as soon as the precipitate subsides, dissolving the phosphate in the least amount of hydrochloric acid, bringing it down again, after dilution, by a faint excess of ammonia, filtering (best, we think, on asbestos, under pressure), washing with faintly ammoniacal water, and igniting as usual.

Many years ago\* a method of precipitating the ammonium magnesium phosphate was advocated by Professor Wolcott Gibbs, which consists, essentially, in boiling the solution of the magnesium salt with microcosmic salt and adding ammonia after cooling, and by which most exact analytical results were obtained. Our experience confirms completely that of Dr. Gibbs, and we desire to direct attention again to a procedure the advantage of which has, unfortunately, not been broadly known and accepted. Even in the presence of considerable

\*This Journal [3], v, 114.

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amounts of ammonium chloride this process yields a phosphate of nearly ideal constitution if only the boiling be prolonged from three to five minutes. The greater part of the ammonium magnesium phosphate—about 90 per cent—forms in this process before free ammonia is added, and the ammonium which enters the phosphate thus formed is derived from the microcosmic salt, which must become correspondingly acidic. Under these conditions, the tendency to form an insoluble ammonium magnesium phosphate richer in ammonia and poorer in magnesia than the normal salt, does not develop. In the process of Dr. Gibbs, as well in the modified precipitation process in the cold, the use of the faintly ammoniacal solution and wash-water is sufficient and advantageous.

In the precipitation of a soluble phosphate by magnesia mixture the tendency of the precipitant and that of the ammonium salt are antagonistic, so that the effect of the latter salt is somewhat masked, though manifest. This opposition of effects has been noted by Mahon,\* who, though regarding the actual attainment of an exact balance as uncertain, ventures the opinion that accurate results should be attainable by the careful relative adjustment of the proportions of the precipitant and ammonium salt. Mahon claims to get the best results by a very gradual addition of magnesia mixture to the ammoniacal solution of the phosphate containing about sixteen per cent of ammonium chloride, strong ammonia being added subsequently. From our observations, however, recorded in section C of Table VI, it appears that the method of introducing the magnesia mixture gradually into the ammoniacal phosphate (taken in quantity sufficiently large to give unmistakable indications) produces a precipitate deficient in magnesium and so leads to errors of deficiency in the phosphorus indicated. The use of strong ammonia, moreover, we have shown to be both unnec-essary and disadvantageous. Our experiments go to show that good results may be expected when the solution of the phosphate containing a moderate excess of the magnesium salt and not more than five to ten per cent of ammonium chloride is precipitated by making it slightly ammoniacal, the precipitate being washed in slightly ammoniacal wash-water. In general, however, and especially when more ammonium chloride than this proportion, or more magnesium salt than twice the amount theoretically necessary, is present, it is safer to decant the supernatant liquid from the precipitate (through the filter to be used subsequently to hold the phosphate), to dissolve the precipitate in a little hydrochloric acid and reprecipitate by dilute ammonia, washing with faintly ammoniacal wash-water.

\* Jour. Amer. Chem. Soc., xx, 445.

Walker—Crystal Symmetry of the Mica Group. 199

ART. XX.—The Crystal Symmetry of the Minerals of the Mica Group; by T. L. WALKER, Assistant Superintendent Geological Survey of India.

FROM the time that the symmetry of crystals was determined exclusively by the aid of goniometrical measurements, there has been a constant degradation of crystals from systems of higher symmetry to those of lower symmetry. Many substances which were once regarded as tetragonal are now looked upon as rhombic; others that were supposed to be rhombic have been shown to be monoclinic, while monoclinic has fre-quently given way to triclinic. The movement has always been downward, lower symmetry replacing higher. This has been due in a small measure, to the improvement that has been made in goniometers, but principally to the progress of physical investigation of minerals. At first it was considered remarkable that the optical properties of cubic crystals should be strikingly different from those of tetragonal and hexagonal crystals, which in turn differed widely optically from rhombic, monoclinic and triclinic crystals. At the present time, however, physical crystallography is looked upon as so important that no crystal can be admitted to any crystal system till it has been examined as to its optical, thermal, electric and cohesive, as well as to its geometrical properties. Only when the physical and morphological properties agree in every respect, is it safe to assign a crystal to a particular system. The degradation caused by placing physical and morpholog-

The degradation caused by placing physical and morphological examination of crystals on equal footing, found its climax in the writings of Mallard,<sup>\*</sup> who seems to have concluded that all crystals are composed of asymmetric particles which may by twinning simulate higher grades of symmetry—sometimes we can detect this twinning geometrically or physically, but even when we cannot detect it, we are to suppose it to exist on a scale so fine that our means of examination are insufficient.

The study of etching figures as an indicator of crystal symmetry, is one of the newest means discovered by the physical crystallographer. This method is often so much more delicate than even the optical method that it points to wholesale degradation. Not only is it much more delicate than the optical method, but it can often be used when no conclusion can be obtained by any other means. There have been many protests against admitting the evidence of this latest and most radical witness, as is exemplified by Brauns, when he says: "Würde

\* E. Mallard, Explication des phénomènes optiques anomaux, Paris, 1877.

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man in dieser Weise die Form der Aetzfiguren unter allen Umständen als ausschlagend ansehen, so würde es bald dahin kommen, dass man nur noch asymmetrische Krystalle kennt."\* It may be urged, however, that etching figures are always in agreement with the optical properties, and, so far as we can test them by other reliable methods, they are found to be in agreement.

Few minerals better show this tendency to degradation from higher to lower symmetry than do the minerals of the mica group. The difficulty in determining the crystal system of the micas by goniometrical measurements is seen in the way in which very eminent minerologists have differed : Marignac and Kenngott held that some micas were hexagonal, and others monoclinic. Senarmont considered them all as rhombic; the late J. D. Dana at one time looked upon them as partly hexagonal and partly rhombic; Leydolt found the etching figures on muscovite cleavage plates to be symmetrical about only one line, and concluded that the micas were rhombic, but hemimorphic about the brachydiagonal. In 1875 Tschermak observed that the optical axis is not exactly at right angles to the basal cleavage and concluded that the micas were monoclinic. The only further degradation possible for the minerals of this group was suggested by Wiik, + who observed that the etching figures on basal cleavage plates are often asymmetric and concluded that at least part of the micas were triclinic. These results of Wiik, though well known, have not led mineralogists to look on the micas as triclinic: at present all text-books describe the micas as monoclinic. The object in writing this paper is to emphasize the conclusions of Wiik by giving addi-tional evidence in favor of regarding some, at least, of the micas as triclinic.

We are accustomed to speak of two classes of micas: 1st, those whose optical plane is parallel to the clinopinacoid, and 2nd, those whose optical plane is at right angles to the clinopinacoid. As the six-rayed percussion figure has one ray parallel to the clinopinacoid, we may determine the crystallographic orientation of crystal fragments by selecting that ray as clinopinacoidal which is either parallel to or at right angles to the optical plane. While examining a specimen of rubellan from the Eifel in this way to determine its orientation, it was observed that the optical plane was neither at right angles nor parallel to any ray of the percussion figure but inclined to one of the rays at an angle of about seven degrees. This led to wider examination of micas and to the following results.

\* R. Brauns, Die optische Anomalien der Krystalle, Leipzig, 1891. † Öfvers. Finska Vet. Soc. Förh. 1880.

## Phlogopites.

The measurements were made on the stage of an ordinary petrological microscope and may be considered accurate to degrees but not to fractions of a degree. The majority of the specimens examined were cleavage sheets, either without crystal edges or with edges which were too rough for exact measurement. All those with sharp crystal edges showed that the edge 001,010 is parallel to one of the rays of the percussion figures, so that, where good edges were absent the divergence of the optical plane from the commonly accepted position was measured against that ray of the percussion figure which was nearest to being parallel to it. The divergence for any one specimen varied with different sheets and for different parts of the same sheet. Cleavage fragments about half a millimeter thick often showed no divergence whatever, but when split to, say a fourth of that thickness, very considerable divergence was noted, some thin cleavage fragments from one and the same crystal showing very much more than others of the same thickness. This, though apparently true in most cases, is particularly plain in the case of small amber-colored transparent crystals from crystalline limestone from Upper Burma, which at a thickness of 1<sup>mm</sup> generally show no diver-gence, but thin plates, about a tenth of that thickness, show a maximum divergence of 11° 30′. The position of the optical plane on one of these Burmese crystals is shown in fig. 1, p. 204. The maximum observed divergences on phlogopites are shown helow

	Maximum observed.			
Locality.	Divergence.	Angle $\chi^*$	. Materi	al used.
Canada.				
Templeton, P. Q.	9°		Cleavage :	fragments.
South Burgess, Ont.	13	61° 53′	"	**
United States.				
Winchester, Pa.	17		6.6	4.4
De Kalb, St. Lawrence Co., N. Y.	6 20'	61 30	64	6.6
Pierrepont, "	4 20		44	66
Rossie, "	2 30	60 50	4.6	6.6
Macomb, " "	3 30	63 30	66	4.4
Hammond, "	10 30		Crystals.	
Pope's Mill, Jefferson Co., N. Y.	7 30	63	Cleavage :	fragments.
Muscalonge Lake, N. Y.	8 30		Crystals.	0
Finland.				
Pargas	14°		6.	
	8		44	
India.				
Upper Burma	11°30'	60° 20′	6.6	
Travancore	14	63 14	Cleavage :	fragments.
Merzapur	3	59 20	44	46
Cevlon.				
Radigara	13°	63° 28'	6.6	6.6
	15	62 27	6.6	4.6

\* The angle of the percussion figure opposite the clinopinacoidal edge .-- Vide this Journal, ii, 5, 1896.

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These observations prove that in phlogopite the optical plane is neither parallel to nor at right angles to the clinopinacoid (so called) and compels us to regard this mineral as triclinic, which agrees with the conclusions of Wiik, founded upon the asymmetric etching figures on the basal cleavage plates, as shown in fig. 2 [after Wiik]. The fact that thicker cleavage plates often give no divergence accounts for the common view as to the position of the optical plane being parallel to the The freedom from divergence in the thicker clinopinacoid. plates is to be accounted for by supposing the mica to be twinned polysynthetically in very thin lamellae with (001) as composition face, which is the commonest recognised twinning law for micas, the apparent optical plane in a thick crystal plate representing the average for the different crystal individuals which go to form the cleavage plate. The maximum divergence then becomes the divergence for a sheet which consists of a single individual; those peculiar etching figures, which are somewhat hexagonal in outline with two small inscribed equilateral triangles with their points so arranged as to constitute a six-pointed star, would also be explained on the supposition that one of the triangles represents the etching figures for one very thin individual, and the other triangle the figures for the individual immediately below.

## Biotite.

It is difficult to determine the *exact* position of the optical plane in the biotites, for the optical angle is so small that the hyperbolas of the interference figure scarcely separate when rotated between crossed nicols in convergent polarised light. This difficulty is also increased by the much darker color of the biotites and by their giving much poorer percussion figures against which to measure the divergence in the absence of crystal edges on the plates. A few of the many biotites examined gave definite results.

Divergence.	Material used.
9°	Cleavage fragments of biotite.
5	<i>u u u</i>
9° 30′	Cleavage fragments of lepidomelane.
	· · ·
7	Crystal of rubellan.
	Divergence. 9° 5 9° 30' 7

These observed divergences would refer biotite to the triclinic system which agrees with the etching figures obtained by Wiik reproduced in fig. 3.

## Lithia Micas.

Only about half a dozen specimens of lepidolite and zinnwaldite were available for examination. The optical plane is sometimes parallel to, at other times at right angles to, one of the rays of the percussion figure, but never divergent as in the case of biotite and phlogopite. This is all the more remarkable, for the etching figures obtained by both Baumhauer and Wiik are so very plainly triclinic in symmetry. Wiik's figures are reproduced in figs. 4 and 5.

## Muscovite.

The optical examination shows no evidence for suspecting that this mica is other than monoclinic, as we at present regard it—this agrees with the etching figures of Leydolt, Baumhauer and Wiik. The optical plane is always at right angles to one of the rays of the percussion figure, as is consistent with monoclinic symmetry. Wilk's etching figures are represented in fig. 6.

From the above statement it seems evident that part of the micas are triclinic—biotite, phlogopite, rubellan, lepidomelane lepidolite, and zinnwaldite, while muscovite is either monoclinic, or, if it be triclinic, it is very finely polysynthetically twinned that we cannot find a triclinic individual large enough to respond to the optical or etching method. According to Mallard, these two are the same—monoclinic crystals (so called) are merely very finely intergrown triclinic twins, the symmetry plane of the monoclinic being due to the increase of symmetry which always accompanies twinning. Lévy has suggested that orthoclase or monoclinic potash feldspar is merely a very finely twinned microcline. A similar relation may hold for the micas.

Some observers have referred to the etching figures on the micas as of monoclinic symmetry. The form of the figures depends on the reagent used, its strength and the duration of the action. Though the physical symmetry of the crystals acted upon is always the same, there may be different amounts of symmetry revealed by different conditions, just as alum may be grown in forms which are geometrically holohedral, as is the case if the crystals are formed in neutral or alkaline saturated solutions, but if grown from hydrochloric acid solutions, pyritohedral faces are nearly always present, affirming that all alum crystals are physically hemihedral even when geometrically holohedral. It would be as unsafe to maintain that the micas are monoclinic, because under some conditions certain reagents give etching figures which appear to be monoclinic in symmetry, as it would be to conclude that all alum crystals are physically holohedral because under certain conditions crystals of alum may be obtained which are morphologically holohedral.

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I have to thank Professors F. W. Clarke, Washington, D.C., S. L. Penfield, New Haven, Ct., G. Tschermak, Vienna, F. J. Wiik, Helsingfors, and A. Lacroix, Paris, for their kindness in sending me specimens of phlogopites.

Indian Museum, Calcutta, July, 1898.



### EXPLANATION OF FIGURES.

FIGURE 1. - Cleavage plate from a crystal from Upper Burma, showing the positions of the percussion figure and optical plane.

FIGURE 2. — Etching figures on phlogopite from Pargas, obtained by hydrofluoric acid. [After Wik.]\*
FIGURE 3. — Etching figures on biotite obtained by hydrofluoric acid. [After Wik.]\*

FIGURE 4 .- Etching figures on zinnwaldite, showing twinning, obtained by hydrofluoric acid. [After Wiik.]\*

FIGURE 5.—Etching figures on rose-red lepidolite from Mursinsk, obtained by action of hydrofluoric acid. [After Wiik.]\* FIGURE 6.—Etching figures on muscorite from Kimito, obtained by action of

hydrofluoric acid. [After Wiik.]\*

\* loc. cit.

 ART. XXI. — Descriptions of imperfectly known and new Actinians, with critical notes on other species, IV; by
A. E. VERRILL. Brief Contributions to Zoology from the Museum of Yale College, No. LXI.

Family PARACTIDÆ. (Continued from p. 146.)

Raphactis Caribæa, sp. nov. Figures 17, A, B, page 146.

Base amplexicaul, surrounding completely the branch of a gorgonian, the two lobes united beneath by suture. The axial line of the stomodæum lies across the branch, in the type. Column low, its surface covered by slightly raised elevations, due apparently to wrinkles, their surfaces smooth; a few small warts are scattered near the collar, which is thickened and has about 30 small, short, crowded, longitudinal ridges; their lower or outer end is largest and most raised. Tentacles numerous, about 72, crowded in four or five rows, moderately stout, tapered, entirely retractile. Mesenteries numerous, thin, about 36 pairs join the outer part of the disk, where some of the smallest bear small gonads. About 12 pairs join the upper part of the stomodæum, but lower down there appear to be only six perfect pairs, most of which are fertile, if not all. Their longitudinal muscles are broad and very thin.

Height of column of contracted specimen, 4<sup>mm</sup>; longest diameter 11<sup>mm</sup>. Color unknown.

Off St. Vincent, W. Indies, 124 fath., Blake Exped., on a brown gorgonian.

## Stomphia Gosse, 1859.

Carlgren, op. cit., p. 80, 1893.

This genus, established for *S. Churchiæ* alone,\* has been studied anatomically and histologically by Carlgren. It is very nearly allied to what I consider typical *Paractis.*<sup>+</sup> It has a

\* Paractis vinosa McMur., op. cit., 1894, p. 167. appears to be related to Stomphia. The number of tentacles is said to be 64, but "the mesenteries are 32 in number, 16 being perfect" (p. 164), and "only the imperfect mesenteries are goonphoric." The number of tentacles given would indicate the presence of 32 pairs of mesenteries, which Prof. McMurrich informs me is the case, an error having occurred in his description. The agreement with Stomphia is therefore close, except that in our larger examples of the latter the perfect mesenteries are also goonphoric. Combined for McMurrich work on cit. 1893. In 124 seems also related rather

Cymbaclis faculenta McMur., op. cit., 1893, p. 174, seems also related rather closely to Stomphia, but has thicker mesogleca, fewer tentacles, 12 pairs of perfect mesenteries, and a feebler sphincter than the type.

+1 do not consider *Paractis excavata* Hert, a true *Paractis*. The latter name should be restricted to such plain forms as agree externally with *P*. *impatiens* (**Dana**). The latter is the first species named by Edw. and Haime and should be the type if it prove, when anatomically studied, to be a paractid. If not, then some of the other named species of similar form should be taken as the type. *P*. *nivea*, described below, is such a species, but cannot be taken as the type. for it

smooth wall, much thickened at the submarginal fold. There are 16 to 24 pairs of perfect mesenteries, the number being variable; their longitudinal muscles are thin and diffuse. The perfect and part of the imperfect mesenteries are gonophoric, in the type. Tentacles are numerous and rather stout.

### Stomphia carneola (Stimp.) Ver. Figures 24, 24a-24d.

Actinia carneola Stimpson, Invert. Grand Manan, p. 7, 1852.

Rhodactinia Davisii (var. 4) Verrill, Revision Polyps E. coast U. States, pp. 19, 20, 1864.

? Stomphia Churchiæ Gosse, Ann. Nat. Hist, Ser. III, vol. iii, p. 48, 1859; Actinol. Brit., p. 222, pl. viii, fig. 5, 1860. Andres, op. cit., p. 369, 1884. Carlgren, Kongl. Svenska, Vet.-Akad. Handl., xxv, 2, p. 80, pl. i, viii, ix, x

(anatomy and histol.), 1892.

? Stomphia coccinea (Müll.) Carlgren, op. cit., appendix, p. 138 (not Sagartia coccinea Gosse, perhaps not Müller's sp.)

Column and base very versatile in form; the base may be broadly expanded or much contracted; and when detached may become small and puckered or swollen and conical. Column may be cylindrical, or almost hour-glass-shaped, or bottleshaped, these changes taking place very rapidly. The wall is smooth in expansion, more or less wrinkled when contracted; there are neither verrucæ nor suckers; a distinct thickened marginal fold or collar may be formed in contraction. Tentacles rather long, tapered, moderately stout, versatile, often perforated, banded; 96 or more in the larger specimens, in two or three crowded marginal rows, the outer ones distinctly shorter and smaller. Disk very changeable, convex or concave. Mouth often raised; siphonoglyphs two; lips with numerous (about 14) small folds on each side.

Color variable, usually bright and translucent; column generally pale pink or flesh-color, irregularly splashed and mottled with rose red, carmine, or scarlet, except just below the margin, where there is usually a zone without spots; sometimes the whole surface is plain flesh-color, or pale greenish white. Tentacles usually pale pink or flesh-color with three bands of rose-red or carmine, of which the distal occupies the tip; from the proximal band a narrow line of red usually runs along each side of the base to the outer part of the disk, where it may form a short radial line; but these are often interrupted, so as to form a circle of red spots on the disk; another circle of small red spots usually occurs near the mouth. There is usually a flake-white spot at the inner base of each tentacle.

A. excavata was taken in 1375 fathoms by the Challenger.

was not originally referred to the genus by Edw. and Haime. The same is true of P. Peruviana (Less.), adopted as type by Audres.

Alloactis, new genus. Type A. excavata (Hert.). Paractidæ with the circular muscles of the tentacles unequally developed at the base, it being much thick-ened on the inside. Wall sulcated. No mesenterial stomata.

The ground-color of the disk is usually pale pink, but it may be pale cream-color or greenish white. The mouth is nearly always surrounded by a narrow circle of bright rose-red, orange-red, or scarlet on the lips; the angles are usually brighter scarlet or vermilion; inside of mouth pink or pale salmon.

In transverse section the wall and base are very thin. The mesenteries are also unusually thin, owing to the very feeble development of the longitudinal muscles; 16 or more pairs are perfect and nearly equal in the larger specimens, but the number is variable; sometimes 24 or more pairs join the upper part of the stomodæum, or even lower down; but only 16 pairs usually join it at its proximal end; those of the 4th cycle are small and often more or less irregularly developed, in the different sextants. Usually, in the larger specimens, a pair is regularly developed between all the pairs of perfect ones; in the stomodæal region these are about one-third as broad as the perfect ones and have longitudinal muscles. All of the perfect and part of the imperfect ones bear gonads, near the base. Some small ones of the 5th cycle also occur near the base. The sphincter muscle is mesodermal, diffuse, elongated, gradually becoming larger distally, and club-shaped or retort-shaped. The mesogleea is considerably thickened in the region of the sphincter. The two siphonoglyphs are continued downward by a short lobe at each angle of the stomodæum, which is large, with about 16 plications on each side.

Height of column, in full expansion, 2 inches  $(50^{\text{nm}})$ ; diameter of disk about 1.5 inches  $(37^{\text{nm}})$ ; length of longer tentacles about 6 inch (10 to  $15^{\text{nm}}$ ).

Bay of Fundy; Eastport Harbor; Johnson's Bay, near Eastport, Me. Not rare in 8 to 35 fathoms, on stony bottoms. Taken by me in 1861, '63, '64, '68, '70, and 1872.

Specimens of this species were described by me in 1864 (Revis. Polyps, pp. 19 (var. 4), 20) as a variety or young of Urticina crassicornis, which it closely resembles in form and color. At that time, however, I stated that it agreed closely with Stomphia Churchiæ Gosse. The anatomical characters of the latter were, of course, then unknown.

There can be little doubt that S. Churchiæ is identical with our species,\* but the latter name is later than carneola, in case they prove identical when directly compared. It has been thought by some writers that Actinia coccinea Müll. is identical with S. Churchiæ, but of that I cannot judge. Carlgren also takes this view in the appendix to his article, but according to Gosse and others that species is a Sagartia.

\* The slight differences between the anatomical description given by Carlgren and my own are doubtless due partly to the greater size of my specimens and partly to the modes of preparation, and to individual variations.

There can be no doubt of the identity of my specimens with Stimpson's carneola. It not only agrees with his description, but Dr. Stimpson was with me on several occasions when we dredged it at Eastport, Me., in considerable numbers, and he positively identified it as his species, but he, at that time, agreed with me that it probably was a variety of U. crassicornis.



Explanation of figures.

FIG. 22. Raphactis nitida V. A cluster of nine, surrounding stems of hydroids. Somewhat less than natural size, from alcoholic specimens. FIG. 24. Stomphia carneda (St.). Side view of a large specimen, one-half natural size, from life. 24a, Section of same, with 23 perfect pairs of mesenteries,  $\times 2$ ; st, upper part of the stomodæum; d. d, directives. 24b, Longitudinal section of the marginal region of the wall; m, thickened mesoglea of the collar; s, section of sphincter muscle. 24c; 24d, two characteristic forms assumed in life, when unattached, ½ nat. size.

FIG. 25. Epiactis prolifera V. One of the types,  $\times 2$ ; y, young attached to sides.

FIG. 29. Sagartia leucolena V. Partly contracted, showing invagination below margin; a, acontia; from life.

All the drawings are by A. H. Verrill, except 24, 24c, 24d, which are from sketches by the author.

### Paractis nivea (Less.). Figure 16, page 146.

Actinia nivea Lesson. Voy. Coquille, p. 81, pl. iii, fig. 8, 1832. Sagartia nivea Verrill. Trans. Conn. Acad., i, p. 485, 1869 (non Duerden). Aiptasia nivea Andres, op. cit., p. 175, 1884.

The wall in most parts of the column is very thin, but strong and parchment-like, often with smooth satin-like appearance, and when seen with a lens it may appear somewhat fibrous transversely; it shows about 48 mesenterial lines. In contraction it is variously, but rather closely and deeply, transversely wrinkled, showing that it is a much elongated species when in full expansion, The sphincter muscle is rather broad and diffuse, without a very definite outline. The mesoglea is thickened near the summit so as to form a fold in contraction; another fold often occurs lower down, when strongly contracted, the upper part being somewhat invaginated into the lower. In these examples there may appear to be **a** second sphincter, due to the longitudinal contraction.

The perfect mesenteries are usually in 12 pairs, but vary from 12 to 16, and rarely 24 pairs, all of which appear to bear gonads. A variable number of small mesenteries occur between the perfect ones; usually those of the third cycle are well developed and bear gonads, but those of the fourth cycle are very rudimentary and do not bear gonads; small rudiments of the fifth cycle may also occur. The longitudinal muscles of the perfect mesenteries are not very thick, but cover most of their breadth.

Tentacles are very numerous and may be entirely infolded and concealed; in the larger examples there are over 120; they are closely crowded in four or five rows; even in alcohol they are rather long and slender with acute tips; the outer ones are much smaller than the inner. In some alcoholic specimens, preserved for thirty years, the tentacles, when they have been protected by retraction, still retain a reddish brown tint, but others are pure white. The tentacles in a large number are fully exposed. Probably the color is variable in life.

The larger specimens are 15 to  $18^{\text{mm}}$  in diameter; some are 25 to  $30^{\text{mm}}$  long, with a diameter of 8 to  $10^{\text{mm}}$ .

Callao, Peru, on the bottom of an old vessel that had been more than a year in that port. They were mostly living in the interstices of large clusters of *Discina lavis*.

This species looks like a *Sagartia*, but no acontia were found in numerous specimens dissected, hence I refer it to *Paractis*.

## Subgenus Archactis, nov. Type A. perdix.

Body nearly smooth in expansion, broad, usually cylindrical; base broad, muscular; margin without distinct fold or thickening, in expansion; disk broad, often undulated; tentacles hexamerous, very numerous (up to 300 or more) in many rows, long, tapered, inner ones far from margin, strongly entacmaeous. Mouth large, with two siphonoglyphs and many lateral folds. Stomodæum with two large basal lobes, making prolongations of the siphonoglyphs; mesogloca of wall rather thick, very flexible, strong; ectoderm soft; sphincter muscle very broad, diffuse, mesodermal, moderately thick distally. Mesenteries hexamerous, very unequal, numerous, with broad, thin, diffuse longitudinal muscles; 12 or more pairs perfect; all the mesenteries fertile, except the directives and the rudimentary ones of last cycle.

The following species differs so much from the ordinary species of *Paractis*, that it seems desirable to make it the type of a generic group, especially as the true type of *Paractis* is not yet determined. It is closely allied to *Stomphia*, but lacks the thick collar and sphincter of that genus, and has a thicker column-wall, lower down. The mesenteries are also more graduated in size.

### Paractis (Archactis) perdix Ver. Figure 26.

Urticina perdix Ver, this Journal, xxiii, p. 223, 1882; Bulletin Mus. Comp. Zool., xi, p. 49, pl. vii, figs. 1. *a*, 1883; Annual Rep. U. S. Fish Comm., xi, p. 534, pl. v, figs. 19, 19a, 19b, 1885.

This large and beautiful species has been pretty fully described as to its exterior, in the works cited above. The tentacles are about 384 in an average specimen. Alcoholic specimen of medium size (diameter of column 1.5 to 2 inches) when dissected had five complete hexamerous cycles of paired mesenteries, and rudimentary ones of the sixth cycle at the periphery of the disk (formula, 6+6+12+24+48+96 = 192pairs). Of these, 94, or all belonging to the first five cycles, except the two pairs of directives, are fertile and bear large gonads; those of the first three cycles are mostly below the stomodæum, while those of the 4th and 5th are in the stomodeal region and extend nearly to the disk; a few of the narrow rudimentary mesenteries of the 6th cycle also bear small gonads, close to the disk. Near the lower part of the stomodæum there are 12 pairs of perfect thin mesenteries, the six lateral primaries being distinctly wider and stouter than the rest. Higher up 12 more pairs (3d cycle) may join the stomodæum and differ but little from those of the 2d cycle; close to the disk some of those of the 4th cycle may join the stomodæum. Lower down those of the 3d and 4th cycles are free and successively somewhat narrower, though still broad, while those of the 5th cycle are much narrower, but all are regular and fertile. The longitudinal muscles are feebly developed on all the mesenteries; even on the perfect ones they are scarcely thicker than the oblique muscles of the opposite side. They extend over the whole breadth of the mesenteries, in a nearly uniform thin layer; the mesoglea is thin with only rudimentary muscle-processes.

The stomodæum is long and large, extending down to about midheight of the body: the two siphonoglyphs are very deep, smooth inside, and extend downward as two large pocket-like lobes, far below the stomodæum, and nearly to the basal disk. They are about half as long and nearly half as wide as the central part of the stomodæum. The free parts of the directive mesenteries are therefore short, narrow, and sterile. The walls of the stomodæum are strongly folded and also have, each, about 36 principal interior plications on each side, nearly all of which are dark brown in color, even after being 16 years in alcohol.

The sphincter muscle is mesodermal, very broad, but not very thick, though it forms more than half the thickness of the wall distally, where it is slightly club-shaped, in section, and blunt at the end; it extends down about half the height of the column, gradually becoming thinner, but locally thickened where the body is most contracted. The wall is flexible, but strong, and of moderate thickness; the mesoglea is rather thick, compact and nearly even; not much thickened at the collar; the ectoderm is rather thick, soft, and so folded by the fine wrinkles, running in both directions that the whole surface often appears to be covered by small wart-like, irregular elevations and papillæ, but the mesoglæa does not rise into them. When living it was smooth, or nearly so, in full expansion. The whole body contracts very much in alcohol, and more so than most species. The collar is but slightly marked even in the contracted specimens, and is not apparent in the live ones; the fosse is also very slight; the margin is tentaculate; the outer tentacles, in alcohol, are very short and conical.

This remarkable species was taken on the Gulf Stream slope, south of Martha's Vineyard, in 62 to 192 fathoms. It lives well in aquaria. One large specimen was kept two months. On one occasion it caught and swallowed a very active golden mackerel (*Caranx*) a foot in length, though several inches of the fish's tail projected out of the mouth for some hours.

### Synanthus mirabilis Ver. Figure 23.

This Journal, xviii, p. 474, 1879; Bulletin Mus. Comp. Zool., xi, p. 48, 1883, pl. vi, fig. 9; Ann. Rep. U. S. Fish Com., p. 534, 1885.

Two alcoholic specimens are now figured; these are united by sutures, side by side, and together surround a branch of *Paragorgia*, like a ligature, making a deep constriction, as in the original types. Tentacles retractile, about 96, rather stout, closely crowded in four or five rows. Wall smooth, and covered with a soft ectodermic layer, which rubs off very easily, leaving a smooth tough surface, slightly sulcated near the summit, and with about twelve principal convergent ridges and some smaller ones alternating. These do not form very definite structures, but are apparently due entirely to contraction. Wall in the region of the collar very thick and firm, with thick mesogleaa. Sphincter muscle mesogleal, much enlarged in the collar, gradually thinning out below.

Mesenteries numerous; about 48 pairs may join the outer edge of the disk, of which some of the smallest bear distally small gonads. Only six perfect pairs join the middle of the stomodæum; these are fertile at base;\* those of the second cycle are nearly as wide and carry large gonads; those of the third cycle are narrow, partly fertile; those of the fourth are rudimentary, except at the outer edge of the disk. The longitudinal muscles of the mesenteries are thin, but cover most of their breadth; they are largest on the lateral primaries. There are two pairs of directives and two siphonoglyphs well developed, but one is deeper. The stomodæum is short. Mouth has six principal folds on each side. No acontia could be found, nor any cinclides.

Height, in alcohol, about  $4^{mm}$ ; diameter of column 10 to  $12^{mm}$ .

Off Nova Scotia, Gloucester fisheries, Lot 534.

The apparent total lack of acontia and cinclides compels me to place this genus in the *Paractida*. Its thickened collar and large sphincter are much like those of *Stomphia* and *Raphactis*. From the last it differs mainly in lacking the thickened, solid, submarginal ridges. Quite likely larger examples might have 12 perfect pairs of mesenteries, as those of the second cycle are wide, in our small specimens. In *Paractida* the number of perfect pairs nearly always increases with age. It also has the habit of *Gephyrea*, but the latter is a Sagartian.

\* Under the name Paractis lineolata (Dana, sp.) McMurrich has described a species with only six pairs of perfect mesenteries, which are also sterile, as in many of the Sayartiade. It had about 96 tentacles and four cycles of mesenteries, while Dana's species had but 24 tentacles, though seemingly of larger size. The differences combined with the fact that Dana's species was from the shore of Orange Harbor, while the Albatross specimes were from N. lat. 8° 16' 30'', in 47 fathoms, render it almost incredible that they can be the same. The latter may possibly be a Sayartian which had lost its acontia, as often happens. To avoid confusion I propose to name it Antiparactis dubia, considering the genus as a doubtful paractid, characterized by the six pairs of sterile perfect mesenteries. It has a large mesodermal sphincter muscle in a thickened submarginal fold of mesogleea, as in many Paractidæ and Sayartiadæ. Its base is not amplexicaul.

## Ammophilactis, gen. nov. Type A, rapiformis (Les.).

Paractid actinians adapted for living in sand, and having a small base, with a round or obtuse limbus in contraction. Wall thin, smooth, tough, often translucent and showing the insertions of the mesenteries. A strong mesogleal sphincter muscle, situated in a thickened part of the wall, which, in contraction, forms a sort of thickened collar, protecting the submarginal, invaginated region; the latter has a very thin wall, covered with numerous minute, rounded, adhesive papillæ, which are not always visible in expansion, but are capable of attaching sand grains. Tentacles tapered, numerous (up to 144 or more), in several rows; the inner ones are far from the margin, larger, but not much longer than the outer ones. Mouth large, with two siphonoglyphs, and with 12 to 16 folds on each side.

Mesenteries numerous; 24 pairs are perfect, and have broad, strong muscles. Imperfect mesenteries of the fourth cycle are also muscular; those of the fifth cycle are feebly developed. The perfect and the larger imperfect mesenteries bear gonads.

Differs from true *Paractis* in its elongated body; the reduced and feeble base; submarginal band of suckers, etc.

### Ammophilactis rapiformis (Les.) Ver. Figures 28, 33.

Actinia rapiformis Les., Proc. Phil. Acad., I, p. 171, 1817.

Paractis rapiformis Edw. & Haime, I, p. 249, 1857. Actinia (?) rapiformis Ver., Revision Polyps, p. 35, 1864; Proc. Boston Soc. Nat. Hist., x, p. 338. Paractis rapiformis Ver., Invert. Vineyard Sd., p. 444. [738]. 1873; this Jour-

nal, III, p. 436, 1872 (descr.). Dana, Coral Islands, Ed. 2, p. 23, cut, 1874. Andres, op cit., p. 262.

Sagartia modesta Dana, Coral Islands, Ed. 1, p. 23, figure, 1872 (non Verrill).

A living specimen found by me in a tide-pool at Outer Island, near New Haven, had the following characters in life : Height of column in extension, about 3 inches (80<sup>mm</sup>); diameter of disk 1 inch  $(25^{mm})$ ; of column  $\cdot 5$  to 1 inch  $(12 \text{ to } 25^{mm})$ ; of base about  $\cdot 5$  inch (10 to  $12^{mm}$ ); length of tentacles  $\cdot 5$  to 1 inch (12 to  $25^{mm}$ ).

The longer tentacles are equal to the diameter of the disk, or even exceed it; they are slender, tapered acute, arranged in several rather crowded rows, the inner series of six are about midway between the mouth and margin; the next six only a little farther outward; the outer ones are only a little shorter, crowded; mouth oblong or elliptical with about 14 folds on each side and a siphonoglyph at each end. Color of column translucent yellowish white with the mesenterial sutures showing through, as paler lines. Tentacles pale gray, with a brownish central line and white tips; each has also, on the inner side, near the end, a flake-white linear median spot or line, with another like it near the middle, and a less evident roundish white spot on the inside, near the base; at the base, on each side, there is a lunate spot of dark brown, the two nearly meeting in front; from each pair of these spots two narrow lines of white, edged with orange, run toward the mouth, but most of them do not quite reach it, but those of the inner rows reach the lips. The disk is grayish white with a halo of pale bluish around the mouth.

This specimen was loosely attached to algæ and probably had been recently washed out of the sand by a storm.

Another specimen from near New Haven (coll. J. D. Dana), of about the same size, preserved in alcohol, has 24 pairs of perfect mesenteries, nearly equally developed, two pairs being directives. Between each pair of perfect ones there is a pair of imperfect ones, about one-third as broad and with strong muscles. In some places rudiments of another cycle can be The longitudinal muscles of the perfect mesenteries found. are strong and extend over most of their breadth, being most thickened at about the inner third. Gonads are borne both by the perfect and imperfect mesenteries. The wall is smooth, thin, but tough, and somewhat parchment-like in alcohol, not much wrinkled, though sometimes fluted longitudinally; the mesenteries show through by translucency, as whitish lines. In contraction, there is a thickened collar below the margin, containing a rather strong, diffuse, mesogleal sphincter muscle. Between the collar and the margin the wall becomes very thin and soft and is covered with numerous very small adhesive papillæ, or suckers.

The mouth has two siphonoglyphs and about 12 principal folds on each side with several other smaller ones, making about 16. The tentacles number about 120; they form four or five rows, the outer ones crowded. The marginal tentacles are smaller than the inner ones, but not much shorter. The basal disk is small, thin, and without a definite margin, the limbus being obtusely rounded.

This is one of the specimens figured by Professor J. D. Dana (Coral Isl., p. 23), but his figure of the mesenteries is entirely diagramatic and was not made from a section.

## Phelliopsis, gen. nov. Type P. Panamensis V. (See p. 144.)

General appearance and habit as in *Phellia*. Column much elongated, but capable of contraction to a short cylindrical, pyriform, or ovate form and of infolding the summit so as to conceal the tentacles, though these are often exposed in preserved specimens. Base with a well developed adhesive disk, about as wide as the column. Cuticle of the scapus thin and closely adherent; integument of alcoholic specimens strongly and closely wrinkled transversely and longitudinally, but without distinct suckers or verrucæ. Submarginal zone without cuticle, plicated in contraction. Tentacles numerous, strongly entacmæous, arranged in several circles.

Mesenteries numerous, hexamerous, very unequal. Six pairs of perfect and fertile mesenteries\* in the type. These have very thick and strong longitudinal muscles. Sphincter muscle rather wide, diffuse. No acontia could be found in several specimens dissected.

The apparent lack of acontia and cinclides compels me to refer this genus to the *Paractidæ*, though it has the appearance of a *Phellia*.

### Phelliopsis Panamensis Ver. Figures 37, 37a.

Phellia Panamensis Verrill, Trans. Conn. Acad., I, p. 490, 1869. Andres, op. cit., p. 127, 1884. Hertwig, Voy. Challenger, vi, p. 81, 1883.

The original description of this species is pretty complete, as to external characters.

The tentacles are in four or five close circles; they vary from 72 to 96 or more; they are strongly sulcated by contraction. In longitudinal sections the stomodæum is short, strongly plicated, and has two siphonoglyphs, while the elongated region below it is largely occupied by the 12 thick and very muscular, perfect mesenteries and the large gonads that they bear, extending from the stomodæum to very near the base (fig. 30, o). The imperfect mesenteries, between these, are very much nar-

\* In my original description of the type species (1869), I stated that the large primary mesenteries were very muscular and fertile, but Hertwig (Yoy. Challenger, vi, p. 81, 1883), when little else had been published in regard to the anatomy of any *Phellia*, expressed more than a doubt as to the correctness of my statement. He wrote, in regard to it: "This so flatly contradicts all observations on the distribution of the reproductive elements in the Actinize that Verrill must somehow have been mistaken." "His observations are of no use for another reason, namely, that he says nothing about the relation of the septa to the eccophague."

As to the last remark, I originally stated that the fertile septa were the large ones, "corresponding to the 12 large inner tentacles" and presumed that every naturalist would know that such mesenteries always join the œsophagus, or are "perfect" to use Hertwig's term. His remark, however, illustrates the uselessness of generalizing as to the internal structure of genera of Actinic that one has not dissected. This has also been well shown in the case of the species referred to Segartia.

As for those actimans that belong to the true Sagartian *Phellina*, it is now known, from the studies of Danielssen and others, that in many of the species the perfect mesenteries are fertile, while in others they are sterile. But it is not known whether these differences may not be due to age or to the season of the year, in many actimans. Perhaps the gonads develop successively on the different cycles of mesenteries in such cases.

The species that Hertwig examined anatomically and described, in the work cited, as *Phellia pectinatus* is not a *Phellia*, but probably belongs to *Chondractinia*.

rower and thinner; those of the second cycle bear smaller gonads, on the upper parts in the stomodeal region. In the larger specimens seven pairs of small imperfect mesenteries intervene between the perfect pairs, there being four hexamerous cycles. The small mesenteries decrease in breadth successively; those of the second and third cycles have well defined thickened, but narrow, muscles; those of the fourth are very narrow.

The wall is flexible, but moderately thick and tough, owing to the well developed but irregular mesoglea, which rises internally into irregular lobulate processes, corresponding to the external plications and wrinkles. It becomes thin and soft in the capitulum. The circular muscle is distinct and continuous, but thin. The sphincter in section is elongated, becoming thicker near the upper edge (fig. 30, s). There is a large mesenterial foramen in the stomodeal region (fig. 30, f').

### Family BUNODACTIDÆ Ver. See No. II, p. 42.

The principal distinction of this family, as compared with Paractide, is the sharply circumscribed endodermal sphincter muscle, which is often only attached to the wall by a part of its outer surface. Its outline, in section, is usually ovate or subcircular, but it varies in form in the same species, according to the degree of contraction. Many Phyllactidæ (Aster-actis) have a similar sphincter, and it is probable that they will hereafter be united with this family. The mesenteries and tentacles may be either hexamerous, decamerous, or octamerous, and are often irregular in number and arrangement.\* There are usually two pairs of directives and two siphonoglyphs, but may be only one; sometimes there are three, or even four. These variations may occur in one species. Perfect pairs of mesenteries are usually 12 or more, and generally all are fertile and strongly muscular. Verrucæ or adhesive suckers are usually present on the column, but not always. No acontia are present.

\* As a rule, the anatomical investigations of actinians have, up to this time, been based on a single specimen, or else on a very few, usually collected at the same season of the year, so that we do not know whether the gonads do, or do not, develop successively on the different mesenteries, even in common species. Moreover, in several cases where considerable numbers of specimens of one species have been dissected, variations often of the most remarkable kind have been found in the arrangement and number of the mesenteries; number of pairs of directives, and of perfect mesenteries; form of the sphinter, etc. This is especially the case in several species of Sagartia, Metridium, Bunodactis, Urticina crassicornis, etc. Of the latter, I have found many specimens hexamerous; both as to tendeles and mesenteries; many others decamerous; some octamerous; and a few irregular or unequally developed on opposite sides. Thus it seems that such internal anatomical characters are often as variable and no more reliable than external characters in certain groups of Actinaria.



FIG. 23. Synanthus mirabilis V.  $\times 2$ ; a, b, sutures between two individuals; c, branch of Paragorgia; d, constricted and broken end of same type

Paracis (Archactis) perdix V.  $\frac{1}{2}$  size, from life, in extreme expansion. Actinostola callosa V.  $\frac{1}{2}$  size, from life, type. Anmophilactis rapiformis V.  $\frac{2}{3}$  size, from life. Stephanauge abyssicola Ver.  $\times 2$ : side view, from an alcoholic speci-FIG. 26. FIG. 27. FIG. 28. FIG. 30.

men, showing cinclides.

FIG. 31. The same, partially expanded; type of Actinauge nexilis V.

FIG. 32. Urticina crassicornis, 1 nat. size; hexamerous variety, from a photograph of a living specimen.

The drawings are by A. H. Verrill; figs. 26, 27, 31 are modified from studies by J. H. Emerton.

## Anthopleura Japonica Ver., sp. nov. Figure 39.

The body is contracted in alcohol to an ovate form, the disk and tentacles being concealed and the base reduced to a small concave area, but it is somewhat mutilated.

Above the middle the wall is covered with fine transverse wrinkles and has unequal vertical rows of concave adhesive suckers. Higher up these are replaced by hollow, round or conical vertucæ, and then by more prominent papillæ, the upper ones becoming lobulated more or less on the outer and under sides by small papillæ. Of marginal papillæ there are 48 rows, larger and smaller, but of these rows only about 36 are prolonged downward by rows of suckers. Some of the marginal papillæ seem to be perforated. The mouth has two siphonoglyphs. Tentacles about 96, rather stout, tapered, arranged in three or more crowded rows. Probably they were rather elongated in expansion. The sphincter muscle is endodermal, rather large, ovate in section, sharply circumscribed.

Mesenteries are in four regular hexamerous cycles, all much thickened; those of the 3d and 4th cycles are successively narrower and smaller; 12 pairs are perfect and nearly equal, including two pairs of directives. All bear strong, thickened, pleated longitudinal muscles; those of the perfect pairs extend over more than two-thirds of their breadth and are thickest about the middle. All, or nearly all, the mesenteries bear large gonads. Some of them are mutilated in the type. The color in life was not noted.

Simoda, Japan, U. S. N. Pacific Expl. Exped.,—Dr. Wm. Stimpson, 1854.

### Bunodactis Manni Ver., sp. nov.

Column more or less cylindrical; base somewhat expanded. Tentacles numerous, in several crowded series, tapered, acute. Column closely covered with numerous, small, rounded verrucæ, arranged in many vertical series.

Color of column usually dark green; verrucæ dark red or brown; disk, around the mouth pink or light red; tentacles dark red.

Height, in expansion 25 to  $50^{\text{mm}}$  (1 to 2 inches); diameter of disk  $35^{\text{mm}}$  or more.

Hawaiian Islands, at and below low water mark in crevices of rocks and attached to stones.

The above description was prepared many years ago, and I now find no specimens in our collections to correspond with it. It was named in honor of my friend, Mr. Horace Mann, a young botanist who visited the Hawaiian Islands to make botanical and zoological collections and who contributed largely to a knowledge of the botany of the islands, but died before his work was finished.

# ART. XXII.—A Study of some American Fossil Cycads. Part I. The Male Flower of Cycadeoidea; by G. R. WIELAND. (With Plates II-IV.)

## Introduction.

THE Mesozoic formations of the Rocky Mountain region, especially around the Black Hills, have furnished few fossil forms of higher scientific interest than the silicified trunks of Cycads there preserved in great perfection. Most of these specimens retain both their external features and internal structure in such minute detail as to make possible a more complete biological study of the entire group than has hitherto been attempted.

There is now in the Museum of Yale University a series of these rare fossils, including several hundred individuals represented by complete, or nearly complete, trunks. For this superb collection of fossil Cycads, Science is indebted to the generosity and untiring zeal of Professor Marsh, who has also given the writer the privilege of examining the entire series.

The exact geological age of these Cycads is still in dispute, but their general position is in the middle Mesozoic, and is most probably Jurassic, as suggested by Professor Marsh in the following statement:

"In the Rocky Mountain region, especially around the margin of the Black Hills, a definite horizon likewise exists, in which great numbers of Cycad trunks are found in remarkable pres-These Cycads resemble most nearly those from ervation. Maryland, found in what I term the Pleurocœlus beds of the Potomac formation. In the Black Hills, the age of the hori-zon has not been accurately determined. \* \* \* Until recently the Cycads of the Black Hills, although of great size and remarkable preservation, have not been found actually in place. In the large collection of Cycads belonging to the Yale Museum, a few have been discovered apparently where they grew, and systematic investigation will doubtless show that the various localities where these fossils have been found around the Black Hills are all in one horizon. The evidence now available indicates its Jurassic age, and suggests that it is essentially the same as that of the Cycad beds in Maryland, which I regard as a near equivalent of the well-known Cycad horizon in the Purbeck of England."\*

\* The Jurassic Formation on the Atlantic Coast.—Supplement.—This Journal, vol. vi, p. 115, August, 1898. See also, the present number, p. 229.

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Prof. L. F. Ward, however, has recorded his opinion that this horizon is Cretaceous.\* While these fossil Cycads must eventually prove of much greater value to stratigraphy than isolated leaves, as pointed out by Prof. Marsh, their present interest is mainly of a structural character.

The living Cycads constitute one of the most ornate and characteristic orders of plants, and, occupying, as they do, a position on the border-land between the higher Cryptogams and lower Phanerogams, their ancestral relationship is of considerable interest in itself, though but little progress has yet been made in working out their phylogeny, owing largely to imperfect knowledge of the fossil forms.

## The Male Flower of Cycadeoidea ingens, Ward.

The male fructification of fossil Cycadean trunks has not hitherto been determined with certainty. An element of doubt surrounds the identity of the separate inflorescences usually held to have been derived from extinct *Cycadeæ*, due to the fact that the Mesozoic Cycads were accompanied by a rich, varied, and closely related coniferous vegetation. In the absence of microscopic characters, it becomes a matter of much difficulty to separate with certainty the fructifications of Cycads from those of some Conifers.

Previous observations on this subject are hence quite limited. Of the supposed fossil Cycadean male fructifications, the pyriform axis described by Williamson<sup>2</sup> has given rise to the most discussion. While it is not necessary to review the literature on this subject here, it may be mentioned that Seward,14 after declaring his belief that the Wealden examples of Williamsonia are generically identical with Bennettites, writes as follows :--"As regards the question of male and female inflorescence, I am unable to recognize any sexual differences in the various examples from the Wealden beds, and there does not seem to be any good reason for regarding the so-called male Williamsonias among the Jurassic specimens as in any way proved to be of that nature. In comparing Williamsonia with Bennettites we have to rely solely on the female inflorescence of the latter plant, and it would seem, so far as our present evidence goes, we have more reason for speaking of Williamsonia as the female inflorescence. As to the nature of the male inflorescence we are still without satisfactory evidence." As will be shown later, the present investigations add a strong degree of probability to this view, if they do not indeed demonstrate its correctness. The reviews of Solms-Laubach," and of Schimper' who alludes to the male axis of Williamsonia as a *Pandanus*-like form, may also be consulted.

\* The Cretaceous Rim of the Black Hills.—Journal of Geology, vol. ii, pp. 250-266, 1894.

The principal loose fossil fruits usually referred to by paleobotanists as male fructifications of Cycadean origin are Androstrobus Baldwini, Saporta,<sup>4</sup> and Zamites familiaris, Corda.<sup>4</sup> Still other and more problematical forms are mentioned by Seward,<sup>4\*</sup> and Solms-Laubach.<sup>8</sup> In no case, however, is the microscopic structure preserved, or a knowledge of these forms at all complete. There is, therefore, no direct basis for comparison between these conical fruits and the capsular male fructification of Cycadeoidea here discussed.



Male flower bud of *Cycadeoidea ingens*, Ward. FIGURE 1.-Diagram of longitudinal section. FIGURE 2.- "transverse"

a group of sori; b, fleshy outer wall; c, central cavity; d, a sorus; e, bract hairs; f, undetermined body; g, basal sorus; h, receptacle; i, involucral bract; k, peduncle.

Both figures are natural size.

The type specimen of *Cycadeoidea ingens*, Ward,<sup>28</sup> which bears the beautiful flower bud here described, is the type of the species, and is a magnificent trunk, nearly perfect, weighing 304 kilograms (671 pounds). In Plate II, it is represented with the flower bud still in position near the summit, where it appears as a conelike projection 3.5 cm in height. Sections of this bud are shown in Plates III and IV. The trunk as seen in Plate II is inclined slightly forward to display the bases of a number of other buds of flowers equally advanced in growth, but not wholly preserved. The main interior structures of this specimen are indicated in the diagrams figures 1 and 2, page 221, based respectively on the photographs of sections shown in Plate III, and in Plate IV, figure 1.

Between this flower bud and the apex of the trunk, distant 15 cm, is a thickly-set mesh of stipulary chaff enveloping a series of finely-preserved, just emergent young leaves, which will be described later.

As removed from the trunk for examination, the general shape of the flower bud was subcylindrical, with a slightly tapering base and a strongly tapering summit. The length, including a considerable portion of the peduncle, was 73 mm, the basal, middle, and apical diameters being 35, 45, and 25 mm, respectively. Laterally it was covered with a series of imbricating involueral bracts, the summits of which had been eroded away. One very noticeable point was the division of the free summit into twelve subequal sectors by radiating lines apparently due to differentiation of tissues.

The upper portion of the peduncle, figure 1, k, is seen to be traversed by a series of fibro-vascular bundles, many of which pass off into the involucral bracts. The latter are covered by a mat of fine hairs quite similar to those borne by the involucral bracts of *Bennettites.*<sup>12</sup> A number of much larger and coarser hairs also arise directly from the peduncle, between the bases of the bracts. The position of the receptacle is indicated centrally by nearly clear quartz, lacking well-defined structure, and peripherally by a shoulder-like offset bearing most of the involucre of bracts.

The basal sori, figure 1, g, are not fully developed, and are irregularly distributed in pockets. Following this absence of arrangement, there is a soral grouping into eleven planes, which successively increase their angle to the floral axis until the terminal series rises vertically. It should be noted, however, that this arrangement is only apparent in longitudinal radial sections, situated at regular intervals with reference to the plan of the flower. In other sections, the sori are crowded together without a traceable arrangement, and the grouping in planes is obscured.

Inside the fleshy spore-bearing portion of the flower, which may for convenience be termed the soriferal axis, is a central cavity of quite regular form, lined by a druse of quartz crystals, figure 1, c, in places resting on a thin layer of chalcedony, which in turn rests on the silicified tissue.

At f, figure 1, is shown an undetermined cylindrical body which has its origin on the receptacle, and curves upward round the base of the soriferal axis, passing half-way up its side. As there are at least ten, if not twelve, of these bodies quite

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regularly distributed in the same relative position, they are in some way connected with the floral plan, though not likely as essential organs.

In figure 2, which is a diagrammatic sketch of the transverse section through the middle of the soriferal axis, based on the photograph shown in Plate IV, figure 1, the plan of the flower is clearly shown. There is first a series of imbricating bracts, the thickly-set hairs of which are not indicated in the sketch. These are in cross section quite thin and scalelike in the middle and upper region of the soriferal axis, especially the interior series. A cross section of the bracts near their origin is seen in Plate IV, figure 2, which represents a section through the base of the flower, about 2 mm below the basal sori. At this height, the cross section of the bracts is approximately of the same form as that of the petioles of the trunk itself.

Inside the involuce of bracts, figure 2, b, is the fleshy integument surrounding the cross area of soral distribution, which is approximately that of a twelve-rayed star, with short points and a hollow center. This is a second clear indication that there is a general plan of twelve, the radial lines of the summit previously mentioned being the first. The sori tend strongly to arrange themselves in tandem pairs parallel to the sides of the twelve points, thus forming an approximation to twelve radial series of from four to six parallel V-shaped groups. Only the examination of a series of successive thin sections now being made will show how far the soriferal surfaces are barren or depart from this arrangement.

It is obvious that the fleshy onter wall extends inward as a homogeneous tissue to form most, if not all, of the soriferal surface. Whether or not these surfaces had any connection with a central axis is obscured by the presence of the central cavity mentioned above. There does not, however, seem to have been any such connection. That there is in any case a series of surfaces which must be regarded as the homologues of sporophylls is a point on which botanists will doubtless agree. The discoveries of Ikeno<sup>33</sup> and Webber,<sup>17</sup> and the investigations of Lang,<sup>24</sup> do not leave any doubt as to the correct terminology of Cycadean inflorescence.

The finer structure of these organs must be treated at another time, though it should be explained now that the sori are composed of from twenty to forty elavate sporangia. Each sporangium is about 1 mm in length and  $\frac{1}{10}$  mm in diameter, and contains 500 or more rounded or subangular bodies not yet completely studied, but undoubtedly the spores or pollen grains.

With regard to the homology of these structures, several facts are worthy of mention. The radial divisions occurring

on the summit are found to persist for a considerable distance downward, and under the microscope are seen to be due to the presence of two lignified layers, a single cell in thickness. They correspond to the twelve vertices of soral distribution mentioned above, and their presence is against the idea that the soriferal axis is derived from the fusion of the sporophylls of a male cone like that, for instance, of *Zamia integrifolia*. Another and much more tenable hypothesis is that the soriferal axis is a series of twelve fused leaves with their sorus bearing pinnules turned inwards.

While it is evident that the inflorescence under consideration represents a development far in advance of that of existing Cycads, the most striking fact observed is the linear distribution of the sori. This is an archaic character most marked in the Carboniferous ferns, especially the *Marattiaceæ*, and their allied forms, living and extinct.

It has probably been the opinion of all botanists, since it was discovered that *Stangeria paradoxa* was a Cycad and not a tree fern, as originally described, that the relationship between the Ferns and Cycads must be an exceedingly close one. All later investigations have tended to strengthen this belief. Scott<sup>20</sup> has recently stated that the evidence in favor of the filicinian ancestry of the *Cycadeæ* must now be considered overwhelming.

It was scarcely to be expected, however, that forms bearing strong testimony on this point should display such a marked combination of advanced as well as ancestral characters.

The further study of the Yale collection promises to afford many new details regarding Cycadean structure and affinity. In addition to the facts presented in this paper, it has been now determined for the first time that the leaf characters of *Cycadeoidea* were approximately those of *Zamia* and *Dioon*, and had the prefoliation of these genera. Moreover, the ancient forms, like the existing Cycads, were dicecious.

In closing, the writer wishes to express his best thanks to Professors Marsh and Beecher for the indispensable aid he has received during the entire course of the present investigations. He is also indebted to Professor Lester F. Ward for valuable suggestions and reference to important literature.

Yale Museum, New Haven, Conn., February 20, 1899.

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### EXPLANATION OF PLATES.

#### PLATE II.

Cycadeoidea ingens, Ward (type). Male plant; showing flower bud at summit. One-sixth natural size.

#### PLATE III.

Cycadeoidea ingens; same specimen.

Longitudinal section through male flower.

For details, see diagram in text, p. 221, figure 1.

Twice natural size.

#### PLATE IV.

Cycadeoidea ingens; same specimen.

FIGURE 1.- Cross section through middle of male flower; showing sori and bracts.

FIGURE 2.—Cross section through base.

For details, see diagram in text, p. 221, figure 2.

Both figures are twice natural size.
## ART. XXIII.—Footprints of Jurassic Dinosaurs; by O. C. MARSH. (With Plate V.)

ONE of the most interesting geological discoveries during the past season in the Black Hills region was a locality of footprints evidently made by Dinosaurian reptiles in deposits of Jurassic age. These footprints are the first found in Jurassic strata in this country. They are all tridactyle, of large size, and were evidently made by some of the great Dinosaurs known to have lived during Jurassic time.

The tridactyle footprints hitherto found in this country were nearly all discovered in the Triassic sandstone of the Connecticut Valley, and, as well known, were at first supposed to have been made by Birds. They have since been discovered in essentially the same horizon in New Jersey and also in New Mexico. In the same strata, many other footprints have been found, and among them numerous similar tridactyle impressions, some of which may possibly have been made by birds, but by far the greater number are evidently of reptilian origin. It is an interesting fact that the bones of Dinosaurs found in this horizon of the Triassic all pertain to animals of moderate size, and none are known large enough to have made any of the gigantic footprints so abundant in the Connecticut Valley.

In the Jurassic formation of this country, on the contrary, the osseous remains of Dinosaurs of large size are especially abundant, and among these were not a few bipedal forms that must have made footprints very similar to the so-called bird tracks of the Triassic, but no footprints of any kind have hitherto been found, although diligently sought for in many localities. The present discovery fortunately supplies the much-desired information on this point, and the specimens already secured promise to throw much light on the life-history of this interesting group of reptiles that were the dominant forms of life during Jurassic time.

When these footprints were first discovered, it was naturally supposed they were of Triassic age, as all footprints of similar character known in this country had been found in deposits of that formation. The great development of red Triassic beds in the same region, and their extension in a broad belt around the Black Hills, where they are generally known as the "red beds," all seemed to favor such a supposition. The character of these beds of red shale and sandstone, all evidently deposited in shallow water, as shown by the ripple marks and other wellknown features, indicated that footprints and other impressions would certainly be found in them if proper search were made, and this will doubtless prove to be the case. The large footprints here described, however, are from a higher horizon, and one well within the limits of characteristic deposits of Jurassic age. Their position in the series of Mesozoic strata encircling the Black Hills is indicated in the diagram, on page 229. This section is designed to show the succession of the principal geological horizons above the Paleozoic in the Black Hills region. The lowest beds here represented are the red beds, already mentioned, which are mainly freshwater deposits, and generally are referred to the Triassic formation.

Next above these comes a series of sandstones, limestones, and shales, containing marine fossils, and named by the writer the Baptanodon beds, from a genus of large swimming reptiles there entombed. This horizon is readily recognized by characteristic marine invertebrate fossils, especially Belemnites, first described from this region about forty years ago by Meek,\* who recognized the importance of the horizon. Above these marine beds are extensive fresh-water deposits of Jurassic age, which the writer has called the Atlantosaurus beds, from a gigantic Dinosaur specially characteristic of the horizon. It is in this series of deposits on the southwestern border of the Black Hills that the footprints here described were found, and it is a point of much interest that here, too, are entombed remains of large reptiles that probably made the same footprints, as will be shown later in the present article.

These Atlantosaurus beds, though overlooked by many geologists, have a great development around the margin of the Black Hills, especially along the southern and eastern borders. The bones of gigantic Dinosaurs mark the outcrop of this horizon at various points. The one best known, the writer explored personally in 1889, near Piedmont, South Dakota, and there obtained remains of an enormous Dinosaur, subsequently named *Barosaurus.*<sup>+</sup> During the past season, important parts of the rest of the type skeleton were secured for the Yale Museum, by G. R. Wieland of that University. With these fossils were found remains of a much smaller species, which may be called *Barosaurus affinis*.

Above the true Atlantosaurus beds is a series of strata of shales and sandstones, the exact age of which is at present a matter of controversy. In this series, there are two or three layers which contain the remains of Dinosaurian reptiles differing somewhat from those below, but especially from those known in the well-defined Cretaceous strata above. The writer has now under investigation for the U. S. Geological Survey, various remains of vertebrate fossils from one of these layers. These fossils, with others secured from different localities in the same region, promise to clear up many of the doubtful points now remaining as to the age of these deposits.

<sup>\*</sup> Proc. Acad. Nat. Sci. Phila., vol. x, pp. 41-59, 1859.

<sup>†</sup> This Journal, vol. xxxix, p. 85, January, 1890.

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The Cycad beds, as they may be termed, from the great number and variety of remains of this group of fossil plants, are abundantly represented around the rim of the Black Hills, apparently at a higher level, but, as the Cycad remains, although distinctive in themselves, have not yet been found absolutely in place in undisturbed strata, their exact position in the series cannot at present be definitely fixed. Part of this series was formerly referred to the Dakota by various geologists, but this reference is fairly open to question, as the writer has shown elsewhere.<sup>\*</sup>

1	Recent. Quaternary.			Tapir, Peccary, Bison. Bos, Equus, Tapirus, Dicotyles, Megatherium, Mylodon.
CENOZOIC.	ry.	Pliocene.	Equus Beds. Pliohippus Beds.	Equus, Tapirus, Elephas. { Pliohippus, Tapiravus, Mastodon, Procamelus, { Aceratherium, Bos, Morotherium, Platygonus.
	Tertia	Miocene.	Protoceras Beds. Oreodon Beds. BrontotheriumBeds	Protoceras, Miohippus, Diceratherium, Thinohyus. ) Oreoton, Epocedon, Jugenodon, Ictops, Hyraco- don, Agriocherus, Colodon, Leptocherus. Strontotherium, Brontops, Altops, Titanops, Titano- (tierium, Mesohippus, Ancodus, Entelodon.
MESOZOIO.	Cretaceous.		Ceratops Beds of Laramie Series.	Ceratops, Triceratops, Claosaurus, Ornithomimus. Mammals, Cimolomys, Dipriodon, Selenacodon, Nanomyops, Stagodon. Birds, Cimolopteryx.
			Atlantochelys Beds of Montana Group.	Atlantochelys, Coniornis.
			Pteranodon Beds of Colorado Series.	Mosasaurs, Edestosaurus, Lestosaurus, Tylosaurus. Pterodactyls, Plesiosaurs, Turtles.
	Jurassic.		Cycad Beds. AtlantosaurusBeds. Baptanodon Beds.	Creads, Cycadeoidea. Dinosaurs, Barosaurus, Brontosaurus, Morosaurus, Dipiodocus, Stegosaurus, Camptosaurus, Alo- saurus, Mammals, Dryolestes, Stylacodon, Tinodon, Clenacodon, Pautosaurus, Belemnites, Trigonia, Pentaernus.
	Tr	iassic.	Red Beds.	A few plants.

GEOLOGICAL HORIZONS ABOVE PALEOZOIC OF BLACK HILLS REGION.

Well-marked Cretaceous strata, showing the characteristic yellow chalk of the Pteranodon beds of the Colorado series, are developed east of the Black Hills, and contain an abundance of characteristic fossils. These deposits the writer personally explored in 1889, and proved their identity with the wellknown series along the Smoky Hill River in Kansas.

Next above come the Atlantochelys beds of the Montana group, well developed, and marked by remains of gigantic turtles, as well as by characteristic mollusca, and other invertebrates. The top of the Cretaceous east of the Black Hills is formed mainly by this group. On the western side of the Hills, the highest Mesozoic deposits are the Ceratops beds of the Laramie. These form one of the best-marked horizons known in any country, as here occur the gigantic horned Dinosaurs of the genus *Triceratops* and others, as well as numerous small Cretaceous mammals and birds.

\* This Journal, vol. vi, pp. 107, 115, and 197, August, 1893. See also, the present number, p. 219.

The Eocene is apparently wanting in the Black Hills region, and the Miocene at many points rests directly on Cretaceous strata. The Miocene is represented by three great horizons, each marked by an abundance of mammalian remains. The Brontotherium beds are at the base, the Oreodon beds next higher, while the Protoceras beds crown the series. The Pliocene is also well developed, as shown in the section, with the Pliohippus beds below and the Equus beds above. Over all, the Quaternary and recent deposits are present, marked by an interesting and characteristic fauna.

Below the series here given, the geological structure of the Black Hills, as well known, is briefly as follows: The central mass is Archean. Outside of this are Silurian strata with the Potsdam sandstone at the base, and limestones of upper Silurian age above. The Devonian is apparently wanting, and the Paleozoic ends with Carboniferous strata, mainly limestones.

The age of the Atlantosaurus beds has long been demonstrated to be upper Jurassic, by the conclusive evidence of vertebrate fossils there entombed. Testimony from other kinds of fossils has not been wanting, and many new facts are coming to light. One noteworthy instance may be fitly recorded here. Remains of the gigantic Dinosaur Barosaurus are characteristic of a definite layer in the Atlantosaurus beds on the eastern side of the Black Hills. Just above this layer, at various localities, there is a thin seam of arenaceous shale filled with remains of minute Ostracoda, and also containing a few fishes. As this seam has a definite position, its fossil contents became important in determining its exact age. Among the fish remains, a perfect tooth was readily recognized as Hybodus polyprion, Ag., a characteristic Jurassic fossil, found in the Dogger, at Stonesfield, England.

A small piece of this shale containing the ostracods was sent to Prof. T. Rupert Jones of London, the highest authority on the subject, and in a letter to the writer, dated February 9, 1899, he reports that in the specimen sent, three species were represented, namely, *Cypridea punctata*, Forbes, *Metacypris Bradyi*, Jones, *M. Whitei*, Jones, all characteristic of the Purbeck. These new facts need no comment. It was already known that two of these species, identified by the same author, occur in the same horizon of the Atlantosaurus beds in Colorado, about four hundred miles further south.

The general characters of the large footprints here described are well shown in those represented on Plate V, one-sixth natural size. In figure 1, page 231, are given the outlines of three other tracks, one-tenth natural size. These are from the same locality and horizon as those on Plate V. They are all reverse impressions, or natural casts, of the surface immediately over the true footprints, which were made in a soft mud that has itself not been preserved sufficiently to retain the imprints originally made in it.

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The interpretation of the various footprints here shown is fortunately a much less difficult matter than that of the huge tridactyle tracks from the Triassic, as in the latter case there was little except conjecture to assist in the investigation. In the present instance, however, it is known that abundant osseous remains of large Dinosaurs are imbedded in deposits of the same age, and in the same general vicinity. Some of these reptiles are known to have been bipedal, and quite large enough to make the footprints now discovered. Moreover, the structure of the feet of some of these animals is sufficiently well known to demonstrate clearly that in walking they must have made footsteps similar to, if not identical with, the fossil specimens here recorded.



FIGURE 1.—Outlines of Jurassic footprints found with those shown on Plate  $\nabla$ a, footprint of large herbivorous reptile; b, footprint of large carnivorous reptile; c, footprint of smaller carnivorous reptile.

#### All the figures are one-tenth natural size.

As to the particular reptiles that made the present footprints, we have a hint in the impressions themselves. Some of these show marks of short and wide toes, suggesting that they were made by the robust feet of herbivorous Dinosaurs. The other footprints show impressions of longer and more slender toes, such as are known in the carnivorous Dinosaurs, which lived at the same time and in the same region as the herbivorous forms, and, indeed, preyed upon them. In Plate V, the large figure on the left evidently represents the footprint of a herbivorous Dinosaur, while the small one on the right, with slender toes, was probably made by a carnivorous form. Of the outline figures above, the one with the thick digital imprints (a) was doubtless made by a herbivorous reptile, while the other two (b and c) appear carnivorous in type.

In selecting from this horizon the known Dinosaurs that might have made the present footprints, it would be safe to say that the genus *Camptosaurus*, especially some of its larger species, may be held responsible for the herbivorous footsteps, while its carnivorous enemy, *Allosaurus*, had representatives to which the more slender impressions may naturally be due. 232 O. C. Marsh—Footprints of Jurassic Dinosaurs.

Other genera of carnivorous Dinosaurs are known to have lived in Jurassic time in the same region where these footprints were made, and among them *Creosaurus* and *Labrosaurus* would probably have left similar tracks, although the structure of their feet is not accurately known. *Ceratosaurus*, another carnivorous form, must also be considered, although not known from the region where the footprints occur, while *Cælurus* is much too small to have made any of the impressions yet discovered. Figures 2 and 3 below show the bones of hind feet of *Camptosaurus* and *Allosaurus*, the Dinosaurs above mentioned.



FIGURE 2.—Left hind foot of *Camptosaurus dispar*, Marsh. FIGURE 3.—Left hind foot of *Allosaurus fragilis*, Marsh. Both figures are one-twelfth natural size.

One point worthy of mention is, that both *Camptosaurus* and several of the carnivorous forms are known to possess, in addition to the three birdlike main digits, a rudimentary toe on the inner side of the hind foot, representing the first digit. This toe, however, was too short to make an impression in ordinary walking on the ground, but might leave a mark where the surface was very soft. No indications of such marks have been found with these footprints, however, and could hardly be expected under the circumstances.

The fossil footprints here described were found by H. F. Wells, in 1898, in the Atlantosaurus beds, on the southwestern border of the Black Hills in South Dakota. The specimens are now deposited in the Yale Museum.

Yale University, New Haven, Conn., February 21, 1899.

EXPLANATION OF PLATE V.

Footprints of Jurassic Dinosaurs from the Black Hills, South Dakota. One-sixth natural size.

#### ART. XXIV. — A new Kansas Meteorite; by HENRY L. WARD, Rochester, N. Y.

IN October last Sam G. Sheaffer, Esq., Attorney-at-Law, of Ness City, Kansas, called our attention to a meteorite that he had in his possession; and which, after some correspondence, he sent to Ward's Natural Science Establishment for the purpose of disposing of it.

Mr. Sheaffer writes that "it was found about a year ago in



the southwest of this, Ness County, Kansas. Was picked up on the side of a draw, i. e., a dry creek, where the surface had been eroded."

In form it is a triangular pyramid with the base set obliquely to its perpendicular.

A mass of some weight had long ago separated from the lower left hand corner, as seen in the figure; but whether before, upon, or after reaching the earth it is now impossible to determine from the fractured part. Several slight depressions appear on the surface, which are

rather too sharply indicated in the accompanying figure. The edges of the nearly plane faces meet in rounded angles.

The meteorite is  $92^{mm}$  in length,  $64^{mm}$  across its widest face, left to right of figure, and  $49^{mm}$  in thickness, measured perpendicularly to the widest, and also largest, face. The termination had been chipped away for the purpose of ascertaining its meteoric character before it was sent to us. The weight of the mass is 417 grams.

This is not a prepossessing meteorite. It entirely lacks the black crust characteristic of aerolites; and so strongly suggested a weathered marcasite concretion that we were at first skeptical as to its meteoric origin. However, tests for iron and for nickel were both affirmative, and a polished chip showed the former well distributed as minute specks through the mass. A complete analysis has not yet been made.

To our knowledge but one other meteorite has been described from Ness County, Kansas. That is the Kansada aerolite designated by the name of the town near which it was found. The locality whence came the specimen under consideration, Section 2, Township 20, S. of Range 21 west, is not marked by a town; and I therefore propose to designate this meteorite as the Ness County.

#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

1. On the Density and Composition of Liquid Air.-Experiments have been made by LADENBURG and KRÜGEL on the density of liquid air of varying composition. The method employed was to weigh a glass rod, whose density at 4° was known, in the liquid air contained in a silvered Dewar bulb, by means of a Mohr balance, and to calculate the density from the loss in weight. At the same time, the composition of the air was determined by Bunsen's method, suitably modified for the purpose. In this way three estimations were made. In the first, the liquid air used was freshly prepared; in the second it had been allowed to stand some time until a portion of the nitrogen had volatilized; while in the third, it was not used until the second or third day after its preparation. The density of sample one was found to be 0.9951, and its content of oxygen 53.83 per cent; that of sample two was 1.029, and its oxygen 64.2 per cent; that of sample three was 1.112 and its oxygen 93.6 per cent. Three facts appear here for the first time: first, that liquid air is lighter than water; second, that the liquid air poorest in oxygen contains over 50 per cent of this element; and third, that the last portions, consisting of nearly pure oxygen, have a density greater than that of liquid oxygen itself. Moreover the density of the gas from this residue was found to be greater than that of gaseous oxygen; it being 1.125 while that of pure oxygen is 1.1056. This is due probably to an admixture either of carbon dioxide or possibly of krypton. From these data the density of ordinary atmospheric air containing 20 per cent of oxygen, and which is not yet obtainable in the liquid state as such, should be calculable, either by geometric or algebraic methods. If the content of oxygen be plotted as abscissas and the density as ordinates, three points are obtained lying nearly in a straight line. Prolonging the line connecting either two of these points till it cuts the ordinate drawn through 20'9 per cent oxygen, values for the density are obtained lying between 0.887 and 0.908. For air free from oxygen, i. e., for pure nitrogen, a value of about 0.84 is obtained, Olszewski having obtained 0.85. Or analytically, assuming that the three points lie on a curve of the second degree such as  $y = a + bx + cx^2$ , the constants a, b and c can be calculated from the experimental values of y the density, and x the oxygen-content, above given. So that the equation becomes

 $y = 0.77892 + 0.00463x - 0.0000115x^2.$ 

For the value x = 20.9 per cent of oxygen, this equation gives as the value of y, the density, 0.8707. Hence were it possible to liquefy atmospheric air without the more rapid evaporation of the nitrogen, it would have a density between 0.87 and 0.90. The authors have applied the same method to the determination of the density of liquid oxygen and of ethylene. Both gases were liquefied in U-tubes immersed in liquid air. Two experiments with differ ent glass rods, gave for oxygen at the boiling point of liquid air (between  $-183^{\circ}$  and  $-188^{\circ}$ ) a density of  $1^{\circ}105^{-1}\cdot108$ ; these values becoming 1'110 and 1'113 when the correction for the change in volume of the glass is applied. Olszewski's value at  $-181'4^{\circ}$ , the boiling point of oxygen, was somewhat higher, 1'110 to 1'137. On passing ethylene gas into a tube immersed in liquid air in a Dewar globe a crystalline mass of solid ethylene is at once obtained, whose melting point was found to be  $-166^{\circ}$ , and its boiling point  $-105'4^{\circ}$  at  $760^{\text{mm}}$  pressure. The density of the liquid ethylene at  $-169^{\circ}$  was found to be 0.6585 and at  $-105'4^{\circ}$ , 0.5710. Methane made from sodium acetate and barium oxide gave variable results, probably from the presence of hydrogen and perhaps of ethylene.—*Ber. Berl. Chem. Ges.*, xxxii, 46, January, 1899. G. F. B.

2. On Semi-Permeable Membranes.-Experiments which have been made by MIJERS have led him to differ from the opinion of Ostwald that semi-permeable membranes are not only conductors like metals but are also "ion sieves." He calls attention to the fact that the copper which is deposited on semi-permeable membranes possesses the nature of a spongy mass rather than a coherent one. If a glass cylinder be closed by a membrane of copper ferrocyanide on parchment paper, and be filled with nor-mal solution of copper sulphate, and then placed in an electrolyzing vessel containing the same solution, the current from two Bunsen cells being passed through it, it is found that no copper is deposited on the membrane during the first half hour, a deposit taking place only when the liquid in the cylinder has become nearly colorless. On weighing the cathode, which is placed in the cylinder closed by the membrane, both before and after the experiment, it is observed that the amount of the deposited copper is in excess, by a considerable amount, of that which was previously contained in the solution in the cylinder, showing that copper must have passed through the membrane. Placing a platinum cathode in acidulated water in a similar cylinder closed by a membrane, and putting this in an electrolytic vessel containing copper sulphate solution, metallic copper is deposited in a few minutes on the cathode; and after four hours the amount of this copper is more than a hundred times that contained in the precipitated copper ferrocyanide on the membrane, which retains its color and is not acted on by the acid. The author's experiments seem to show that semi-permeable membranes are conductors differing entirely from metals. Thus if, in a copper sulphate electrolyzing vessel the anode and cathode are separated by a semi-permeable membrane held between two rings of ebonite, and by a sheet of platinum of exactly the same size as the membrane, no metal is deposited on the membrane when the current passes, the deposit taking place on the platinum near the center, the margin being protected by the ebonite .- Rev. Trav. Chim., xvii, 177, 1898; J. Chem. Soc., lxxiv (ii), 505, November, 1898.

G. F. B.

AM. JOUR. Sci.—Fourth Series, Vol. VII, No. 39.—March, 1899. 16 3. On the Solution of Platinum and Gold in Electrolytes.—It has been observed by MARGUELES that if an electro-magnet provided with a vibrating armature be made to act as a contact breaker to the current from two Daniell cells, an electrolytic cell provided with platinum or gold electrodes being included in the circuit, the metal can be made to dissolve in hydrochloric, nitric or sulphuric acid, or in potassium or sodium hydrate. The solution always takes place from that electrode which is for the time being the anode. It is helped in some way, however, by the discharge current from the magnet, as the current from the battery alone does not effect the solution, neither when continuous nor intermittent.— Wied. Ann, lxv, 629-634, June, 1898. G. F. B.

4. Aqueous Solutions of Metallic Gold.—By treating a feebly alkaline boiling solution of gold chloride with a reducing agent, ZSIGMONDY has shown that a red aqueous solution of metallic gold may be obtained.\* Formaldehyde seems to be the best reducing agent, less satisfactory results being given by acetaldehyde, alcohol and hydroxylamine. Sometimes the solution, instead of being red, is dark purple, violet or bluish black and appears turbid. The solutions of gold are very dilute, only about 0.005 gram of gold to the hundred cubic centimeters. They undergo no change when boiled until reduced to less than half their volume, when they become violet-black and deposit gold as a black powder. The solutions may be concentrated by dialysis, which become intensely red and contain 0.12 per cent of colloidal gold. Solutions of neutral salts and mineral acids change the color to blue and slowly precipitate finely divided metallic gold. Potassium ferrocyanide produces a green coloration, subsequently becoming yellow. Acetic acid gives a violet red and finally a black. Alkalies precipitate blue gold. Alcohol in excess changes the color gradually to dark violet, precipitating the metal completely in a condition in which it is soluble in water. When submitted to the action of a current, aqueous solutions of gold act like other colloids; the metal travels toward the cathode, but does not penetrate the membrane.-Liebig's Annalen, ccci, 29-54, June, 1898. G. F. B.

5. On the Explosion of Mixtures of Methane and Air by the Electric Current.—Extended experiments have been made by COURIOT and MEUNIER on the action first of incandescent wires and second of electric sparks, on mixtures of methane with air in various proportions, the gas being sometimes at rest and sometimes in motion. A mixture of 80 per cent of methane and 20 per cent of air, in motion, could not be fired by an incandescent wire nor even by the spark at the break when the wire fused; though it readily ignited in contact with a flame. If an electric current produces any effect at all on a mixture of methane and air, the only effect is an explosion. But under no circumstances were the authors able to produce an explosion with an incandescent wire. Whenever an explosion was produced it was due to the spark produced at the breaking of the wire. A mixture con-

\* See Faraday's Exp. Res. in Chem. and Phys., p. 411.

taining 9.5 per cent of methane is the most readily explosive. The combustion is complete so long as the methane does not fal below 5.5 per cent. Even with 4.5 per cent slight explosion were noticed. With 12 per cent of methane, the explosibility reaches its maximum limit, no explosion having ever been obtained when the proportion was as high as 12.25 per cent.

In a subsequent paper, the authors state that if the current by which the wire is heated be shunted with a parallel wire, the production of the spark causes no ignition of the gas, if the resistances are equal in the two branches. If the shunt-resistance is high, or on the other hand if this resistance falls below a certain value, the production of a spark always produces an explosion. To avoid an explosion therefore the current strength must not exceed a certain maximum depending on the resistance of the two branches of the conductor.— C. R., exxvi, 750, 901, March, 1898. G. F. B.

6. On a Crystallized Compound of Cuprous Chloride and Acetylene.—It has been pointed out by CHAVASTELON that on treating cuprous acetylide with hydrochloric acid in the cold, an appreciable evolution of gas takes place; due probably to the decomposition on warming of a compound of cuprous chloride and acetylene. Further investigation showed that this compound may be prepared either by the action of acetylene on a solution of cupric chloride in alcohol or in water, in presence of metallic copper, or by passing this gas into a saturated solution of cuprous chloride in dilute hydrochloric acid, at a temperature at or below 12°. By the latter method, which is preferable, large hexagonal crystals are obtained belonging to the orthorhombic system, having the composition  $C_aH_a$ :  $Cu_aCl_a$ . By the former process, silky crystals are yielded, which are liable to contamination by a violetpurple deposit, formed early in the reaction. Both products alter readily on exposure to the air, and are at once decomposed by water or by solutions of alkali chlorides, with evolution of acetylene and the production of the above mentioned violet-purple substance. The crystals dissociate on warming without explosion, producing at 78° a pressure of 262cm. - C. R., cxxvi, 1810-1812, June, 1898. G. F. B.

7. Matter, Energy, Force and Work. A plain presentation of Fundamental Physical Concepts and of the Vortex-atom and other Theories. By SILAS W. HOLMAN, Professor of Physics (Emeritus) Mass. Institute of Technology. 12mo, pp. xiv, 257. New York, 1898 (The Macmillan Co.).—The aim of this book, as the preface tells us, is to present some fundamental ideas and definitions of physics in a plain and logical manner. The subject matter proper is contained in the first part, the definitions and views there given constituting "a sporadic attempt at clear consecutive setting forth of individual thought." The second part consists of speculations on matter and energy. Two new terms are introduced, kinergety and weightal. Kinergety in the abstract sense denotes "the idea of capacity for kinetic energy" and in the concrete sense "the quantity of this capacity." Weightal is defined to be "quantity of substance measured by the equal-arm balance." With regard to the vortex-atom theory, Lord Kelvin writes to the author "I am afraid it is not possible to explain all the properties of matter by the vortex-atom theory alone." "I have not found it helpful in respect to crystalline configurations, or electrical, chemical or gravitational forces." The book contains a thoughtful presentation of fundamental physical concepts and cannot fail to be of much service to those students who desire a philosophic knowledge of modern theories. G. F. B.

8. Uranium Radiation, and the Electrical Conduction produced by it.—A very exhaustive investigation of this subject has been published by Prof. RUTHERFORD of McGill University. Becquerel had stated that the uranium rays differed from the Röntgen rays in this respect, that they can be refracted and polarized. Professor Rutherford cannot find any evidence of refraction or polarization. The theory of ionization adopted by the author supposes that the rays in passing through a gas produce positively and negatively charged particles and that the number produced per second depends on the intensity of the radiation and the pressure. The term ion does not assume that the ion is necessarily of atomic dimensions. These ions are supposed to be carriers of electricity. Prof. Rutherford examines the theory that energy is absorbed in producing the ions and that the absorption is proportional to the number of ions produced and thus depends on the pressure. If this theory is correct he points out that we should obtain the following results:

(1) Charged carriers produced through the volumes of the gas.

(2) Ionization proportional to the intensity of the radiation and the pressure.

(3) Absorption of radiation proportional to pressure.

(4) Existence of saturation current.

(5) Rate of recombination of the ions proportional to the square of the number present.

(6) Partial separation of positive and negative ions.

(7) Disturbance of potential gradient under certain conditions between two plates exposed to the radiation.

The experiments performed by the author indicate that the theory affords a satisfactory explanation of the electrical conductivity produced by uranium radiation. He shows also that the uranium radiation is complex, and that there are present at least two types, which he terms  $\alpha$ - and  $\beta$ -radiations. The character of the  $\beta$ -radiation seems to be independent of the nature of the filter through which it has passed, and passes through all substances tried with far greater facility than the a radiations. The photographic effects are due principally to the  $\beta$ -radiations, except when the uranium compounds are placed close to the photographic plate. The experiments on transparency of metallic plates are not in accordance with those of Becquerel. The absorption of the  $\beta$ -radiation in gases is probably of the same order as that of the X-rays .- Phil. Mag., January, 1899, pp. 109-163. J. T.

#### Geology and Mineralogy.

9. On the Silver Voltameter and its use in determinations of normal elements.—In a contribution from the Reichsanstalt, K. KAHLE discusses the subject and gives the results of a careful inquiry of the electromotive force of a Clark and a Cadmium cell, and a comparison with previously obtained results by means of a Helmholtz electrodynamometer (Wied. Ann., lix, p. 532, 1896) of the electrochemical equivalent of silver. The final value obtained is  $E = 1^{11}183$  mg/sec. which is in accordance with the previously obtained value.— Wied. Ann., No. 1, pp. 1-36, 1899.

10. Absorption of light by a body placed in the magnetic field.-RHIGI discusses the work of investigators who have occupied themselves with the phenomena of absorption discovered by him. It is shown that the Zeeman effect is accompanied by a rotation of vibrations of which the wave lengths are close to those of the radiations absorbed. According to Becquerel and Voigt, one could predict this rotation from the facts of anomalous dispersion. Rhigi does not believe with MM. Corbino and Macaluso that the rotation constitutes the principal cause of the appearance of light in his experiments; for the condition that the phenomena of rotation may be observable, namely, great length of rays of absorption, is not necessary and is even prejudicial. One cannot maintain absolutely that Rhigi's experiments would lead to the discovery of the Zeeman effect. They reveal the existence of a phenomenon less simple-a Zeeman effect together with rota-tions, more or less simple, of vibrations which, it may be, always accompany it. - Comptes Rendus, No. 1, pp. 45-48, January, 1899. J. T.

#### II. GEOLOGY AND MINERALOGY.

1. Recent Earth Movement in the Great Lakes Region; by GROVE KARL GILBERT. (From the Eighteenth Annual Report of the Survey, 1896-97. Part II.)—The question as to the existence at the present time of progressive changes of level between the water and land in the region of the Great Lakes is one not only of great theoretic interest, but also of much practical importance, since a relative rise of the water may have a profound effect upon the value of property on the shores of the Lakes. This subject is discussed by Mr. Gilbert with great care and thoroughness. He remarks upon the earth movements which characterized the closing epochs of the Pleistocene Period, as clearly brought out by the studies of Dr. Spencer, Mr. F. P. Taylor, and others, of the shore lines of the early glacial lakes that covered more or less of the region. He quotes Dr. Spencer (1894) as urging that this change of level has not ceased, and that it will eventually turn the water of the Upper Lakes southward to the Illinois and Mississippi Rivers, leaving the Niagara channel dry. This is one consideration which has weight in the matter.

Another is found in the condition of the estuaries which show

J. T.

a close resemblance to features observed along the subsiding parts of the Atlantic coast, and give an impression that a slow flooding of the stream valleys is still in progress. A third point noted is the accepted fact that the Atlantic coast, south of Connecticut, is subsiding, as has been estimated (Cook) for New Jersey about two feet in a century; while the land about Hudson and James bays has risen (Bell) perhaps five to seven feet in a century. These facts all point in a common direction, warranting the hypothesis that the tilting of the Lake region which went on at the close of the glacial times, as shown by the slopes of old shore lines, is still in progress.

The author notes at the outset a paper by Mr. G. R. Stuntz (1869), in which he argued, in the case of Lake Superior, that there was a gradual rise of water at the west end of the lake, and a fall of the same at the east, referring this to a westward canting of the basin, the western part becoming lower as compared with the eastern.

With this introduction the author goes forward to discuss the plan of investigation, and the data available, with also certain special observations made in 1896. The stations are taken in pairs, the points being so chosen as to most satisfactorily show what change of level, if any, has been going on. An absolute conclusion is difficult to reach, since very few of the observations are above question because of the doubt as to the stability of the individual base levels involved. Still the candor and fairness with which the author weighs the evidence is worthy of all praise and gives his conclusions great value.

He decides that the harmony of the measurements, and their agreement with the predictions of geological data, makes so strong a case for the hypothesis of tilting that it should be accepted as a fact, although some doubts exist concerning the stability of the gauges. The mean rate of change deduced is 0.42 foot to one hundred miles in a century; but this depends upon certain assumptions which he does not regard as altogether probable, and he notes that the change indicated by Stuntz's observations is much more rapid. It would seem then that the assumption is justified that the whole Lake region is being lifted on one side or depressed on the other, so that its plane is bodily canting toward the south-southwest, and that its rate of change is such that the two ends of a line one hundred miles long, and lying in a south-southwest direction, are relatively displaced fourtenths of a foot in one hundred years. Certain general consequences follow from this assumption (eliminating irregularities due to difference of rainfall, evaporation, etc.). Thus, on Lake Ontario, the water is advancing on all the shores. This is also true of Lake Erie, the most rapid change, of eight or nine inches in a century, being at Toledo and Sandusky. About Lake Huron the water is falling more rapidly in the north and northeast. At Lake Superior the water is advancing on the American shore and sinking on the Canadian. Similar relations exist for Lake Michigan, the water falling in the north and rising in the south, at Chicago some nine or ten inches. The ultimate result would be the discharge of the lakes through the Illinois river, the channel of the Pleistocene glacial lake being occupied anew. The high-water lake discharge may begin in 500 to 600 years, for mean lake stage it will begin in 1,000 and after 1,500 it will go on uninterruptedly. In about 2,000 years the Illinois river and Niagara will carry equal portions of the surplus water of the Great Lakes, and in 3,500 there will be no Niagara. The author adds : "The most numerous economic bearings of this geographic change pertain to engineering works, especially for the preservation of harbors and regulation of water levels. But the modifications thus produced are so slow as compared to the growing demands of commerce for depth of water that they may have small importance. It is a matter of greater moment that cities and towns built on lowlands about Lakes Ontario, Erie, Michigan, and Superior will sooner or later feel the encroachment of the advancing water, and it is peculiarly unfortunate that Chicago, the largest city on the lakes, stands on a sinking plain that is now but little above the high-water level of Lake Michigan."

The paper closes with a statement of certain definite plans made for precise measurements at selected stations, for example, at Chicago, Port Huron, Parry Sound, and Mackinaw, which if they can be carried out systematically, must in time lead to a very definite solution of the problem in hand.

2. On the Petrology of Rockall Island.—Professor J. W. JUDD has recently described a remarkable rock under the name rockallite from the isolated point which rises from a shoal above the waves of the North Atlantic 240 miles west of Ireland. It appears to be a remnant of an intrusive sheet resting on sediments. The tiny islet has long been known under the name of Rockall. Prof. Judd's paper forms one of a series of memoirs descriptive of this remarkable island.\* As this rock is of very interesting character a brief description will be of interest to petrographers.

It is of granitic character but with an approach to a porphyritic structure in places owing to the idiomorphic outlines of the lathshaped feldspars, which allies it to the granite porphyries. In composition it is very simple, being made up of ægirite, albite and quartz in the following proportions: ægirite 39, quartz 38, albite 23.

The ægirite is found in larger crystals and in fine needles, and shows at times brown acmite zones. The albite is twinned according to the albite and Carlsbad laws and its phenocrystic sections contain ægirite. The quartz is the last mineral to form and fills the interspaces. A little apatite and soda amphibole are present. The specific gravity varies from  $2\cdot9-2\cdot7$ . In the more porphyritic

<sup>\*</sup> Notes on Rockall Island and Bank with an account of the Petrology of Rockall, and of its winds, currents, etc.: with reports on the Ornithology, the Invertebrate Fauna of the Bank and on its previous history. Transactions of the Royal Irish Academy, vol. xxxi, Part III, pp. 30-98, plates ix to xiv.

variety a little groundmass is present. The chemical analysis gave these results :

= 99.83

SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub>  $Fe_2O_3$ MnO NiO MgO CaO Na<sub>2</sub>O K<sub>0</sub>O  $P_{2}O_{5}$ 73.60 4.70 13.10 ·93 .06 .11 .37 6.96 tr. tr.

In this TiO<sub>2</sub> and FeO were not determined. The analysis is remarkable for the low alumina, the high iron and the absence of potash. In these respects it is most closely related to the grorudites of the south Norway region and to some of the lavas of Pantellaria. From them it differs however in its granitic structure, the higher proportion of ægirite and in the character of its feldspar. The introduction of its name as a varietal one in the alkaline granite group is therefore justified. L. V. P.

3. Recherches géologiques et pétrographiques sur le massif du Mont Blanc; by L. DUPARC et L. MRAZEC (Mem. Soc. de Phys. et Hist. Nat. de Genève, xxxiii, No. 1, 4°, pp. 227, pl. 33, 1898).—In this great work the first part is devoted to a full account of the topography of the Mont Blanc massif and the position it occupies in the system of the Alps. Then follows a very full petrographic investigation of the eruptive rocks and of the relations existing between them followed by a similar account of the crystalline schists which accompany them. A very large number of analyses of the types described is also given.

The fourth part is devoted principally to the description and theory of the metamorphic phenomena produced by the protogine in the crystalline schists with which it is in contact. The next part is a description of the sedimentary rocks involved in the mass and the whole concludes with a discussion of the tectonic processes and of the folds and uplift which they have produced. In addition to the large number of half-tone plates of scenery and rock sections, a number of excellent geologic sections in color are given. The authors regret that the expense prohibited an accompanying publication of the geologic map they have made, a regret in which all readers will agree with them.

The whole is an exhaustive monograph and gives the results of an enormous amount of painstaking labor both in the field and in the laboratory. It is one of the most important contributions to Alpine geology which has appeared in recent years. L. v. P.

4. Native Silver in North Carolina; by G. F. KUNZ. (Communicated.)—In June, 1898, while some mining was being carried on at the West Prussian Mining Company's land, at Silver Hill, near Livingston, Davidson Co., N. C., an interesting deposit of native silver was brought to light. An inclined shaft was sunk to a depth of 75 ft., near a mixed mass of sulphides of lead, zinc, copper and iron, associated with a vein of green rock, in places weathered and decomposed almost to a white clay. In and through this, a soft, slaty mass of native silver was found, disseminated'in grains and plates presenting the appearance of having been absorbed in the interstices of the slate, and varying in size from minute grains and scales of metal to pieces several square inches in area, and up to one-fourth of an inch in thickness; the largest single mass weighing, with some of the adherent slate, about 5 lbs.

The sulphides are not crystallized; but appear to be almost homogeneous and are comparatively rich in lead and zinc, an average assay yielding 35 per cent of zinc and 20 per cent of lead, with 25 ounces of silver and one-fourth an ounce of gold to the ton. An assay made by Dr. A. R. Ledoux proves the silver to be almost absolutely pure, containing only 1 per cent of native gold. The silver occurs in veins, with more or less open spaces, and showing very minute crystals on the upper and lower part of the vein. A near view, side-ways, reveals it to be in fibrous masses and ropes, having all the appearance of sweating out of the rock, probably a result of the decomposition of the chloride, leaving the silver in fine, fibrous masses, varying from short ropes 10 millimeters in diameter to the fineness of a hair.

The specimens and information were kindly furnished by Wyndham H. Wynne, of Glendalough, Ireland.

5. On the occurrence of polycrase in Canada; by G. CHR. HOFFMANN. (Communicated.)-Fine examples, of what on examination by Mr. R. A. A. Johnston proved to be polycrase, have been found by Mr. C. W. Willimott, in the township of Calvin, district of Nipissing, in the province of Ontario. It occurs here in the form of crystalline masses-one of which weighed rather more than seven hundred grams-associated with xenotime, a highly altered, cleavable massive form of magnetite, and small quantities of a brownish-red spessartite, in a coarse granite vein, composed of quartz, microcline, albite or oligoclase, muscovite and biotite, which is there found cutting a reddish, fine-grained, hornblendic gneiss. The mineral has a pitch-black colour; an uneven, in parts subconchoidal fracture; a resinous lustre; is brittle; and affords a grayish-brown streak. Its specific gravity, at 15.5° C., is 4.842. A very carefully conducted qualitative analysis showed it to contain-Niobic oxide, large amount; tantalic oxide, somewhat small amount; titanic oxide, large amount; yttrium oxide, somewhat small amount; thorium oxide, small amount; stannic oxide, trace; cerous oxide, small amount; lanthanum oxide, small amount; didymium oxide, small amount; uranous oxide, small amount; ferrous oxide, small amount; magnesia, trace; water, very small amount. Zirconia was sought for, and found to be absent.

6. The Kaolins and Fire Clays of Europe, and the Clayworking Industry of the United States in 1897; by HEINRICH RIES. From the Nineteenth Annual Report of the U. S. Geological Survey, 1897–1898.—Professor Ries has here brought together a large amount of important information on the occurrence, composition and general use of the clays from the important localities in Europe. This is chiefly based upon the personal observations of the author during recent visits to the localities themselves. The value of the paper will be appreciated when the importance of the industry in this country is considered, and at the same time the very impertent and fragmentary amount of information which has already been published in the various technical journals. A brief summary is also given of the clay industry in the United States.

7. On the Origin of the Gases evolved on heated Mineral Substances, Meteorites, etc.-A paper by M. W. TRAVERS in the Proceedings of the Royal Society (No. 405) discusses the evolution of gases from various minerals and meteorites, especially with reference to their origin. His conclusions are somewhat at variance with those ordinarily accepted, in that the experiments go to prove that in the majority of cases, the gas evolved under the influence of heat is the product of decomposition or interaction of non-gaseous constituents present in the substance under examination. It is conceded that compact minerals do inclose carbon dioxide and hydrocarbons as easily liquefiable gases; but the analogy cannot be extended to gases such as hydrogen and helium in connection with readily cleavable minerals like chlorite, mica and cleveite. The special importance of the conclusions here reached lies in the fact that it invalidates the conclusion reached in regard to the origin and history of the substances in question. This is partly true in the case of meteorites.

#### III. BOTANY AND ZOOLOGY.

1. Symbolæ Antillanæ seu Fundamenta Floræ Indiæ Occidentalis; editit Ignatius URBAN. Vol. I, Fasc. I continet: I, Ign. Urban : Bibliographia Indiæ occidentalis botanica, pp. 3-192. Berolini, 1898 (Fratres Borntraeger). - Within recent years, Professor Urban has published numerous papers dealing with the flora of the West Indies. His articles have appeared in various German journals and have of necessity been somewhat scattered and disconnected. It is now his intention to publish the further results of his studies in this domain in a series of papers under the above title, the various fasciculi to appear at indefinite periods and to deal mainly with difficult or neglected families, the description of new genera and species and the geographical distribution of plants on the islands. This first paper contains a list, arranged alphabetically according to authors, of the numerous works dealing with the botany of the West Indies, but it is much more than a mere enumeration. After each title, which is given in full and also in a shortened form suitable for citation, follows an abstract of its contents, and, in the case of taxonomic papers, an indication as to where the plants described are at present preserved. Especially valuable are the many references to works published in Spain or in the West Indies themselves, many of which are difficult of access and therefore little known to botanists.

A. W. E.

2. Plant life: considered with special reference to form and function; by CHARLES REID BARNES, Professor of Plant Physi-

ology in the University of Chicago; pp. x + 428, with 415 figures in text. New York, 1898 (Henry Holt & Company).-As stated in the preface, Professor Barnes' text-book attempts "to exhibit the variety and progressive complexity of the vegetative body; to discuss the more important functions; to explain the unity of plan in both the structure and action of the reproductive organs; and finally to give an outline of the more striking ways in which plants adapt themselves to the world about them." The four parts into which it is divided deal accordingly with the following subjects : I. The Plant Body; II. Physiology; III. Reproduction; and IV. Ecology. It will be seen, therefore, that the book is very comprehensive in its plan and that most of the great divisions of modern botany receive a certain amount of attention. The topics are, with few exceptions, treated according to recent researches, but the very comprehensiveness of the subject makes great conciseness necessary, and it is to be feared that some of the statements are so concise as to be obscure, at least to pupils from thirteen to eighteen years of age, for whom the book is pri-marily intended. The arrangement of the subject-matter, also, although logical, might readily lead the pupil to believe that a plant is composed of certain definite and more or less disconnected parts, instead of being an organism whose parts, although distinct enough from a formal standpoint, are nevertheless so intimately connected and so dependent upon one another that they form a most definite whole: in other words, that botany is the study of plant-organs rather than of plants. For example, under "simple sporangia" on page 316, the sporangium of Mucor, the ascus of Peziza and the tetrasporangium of Polysiphonia are described in due order; but, if we wish to find other facts about Polysiphonia, we must look on page 32, for a description and figures of the vegetative structure, and on page 289, for a figure of the cystocarp: and other, even more striking examples might be quoted. The short section on ecology, which, as the author implies, is largely abridged from two recent German works, is an interesting feature of the book, and, it is to be hoped, will demonstrate to teachers how very useful this important department of botany might become for purposes of instruction. At the close of the book are five appendixes in which laboratory directions, lists of apparatus, reagents and reference books, and a very brief outline of classification are given. A. W. E.

3. Rhodora: Journal of the New England Botanical Club, Vol. I, Nos. 1 and 2, January and February, 1899. Boston and Providence.—After mature consideration, the New England Botanical Club has decided to publish a journal devoted to the interests of New England botany. The first two numbers have recently appeared, and the editorial announcement states that the journal will devote special attention to matters connected with the geographical distribution of New England plants and to the revision of difficult or misunderstood groups of species. It also states that "not only flowering plants, but ferns, mosses and thallophytes will receive their proportionate share of attention." Some idea of the character of the matter presented may be obtained from the following titles, selected from the numbers before us: rattlesnake plantains of New England (with plate); notes on algæ; a new wild lettuce from Massachusetts (with plate); notes on some fleshy fungi found near Boston; some plants about Williamstown; fairy-rings formed by Lycopodium; bryophyte flora of Maine.

4. Catalogue of the Lepidoptera Phalaence in the British Museum, Vol. I, Syntomidæ; by George F. HAMPSON. With 17 colored plates. 8vo. London, 1898.-This is the first volume of a proposed catalogue of all the known genera and species of moths. The introduction contains a brief statement of the external structure of the Lepidoptera and an analytical key to the families. This is followed by the account of the Syntomidæ, a family of very pretty moths which is confined almost exclusively to tropical and subtropical regions. Nearly twelve hundred species are described and the genera and subgenera illustrated by 285 figures in the text. The plates contain about 370 beautifully colored illustrations of new or hitherto inadequately figured species, but, as they are not essential to the plan of the work, they are issued separately, so that the text may be sold at a much less price than if the plates were combined with it.

#### IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Report of S. P. Langley, Secretary of the Smithsonian Institution, for the year ending June 30th, 1898.—The annual reports of the working of the Smithsonian Institution are always of much interest, because of its remarkably wide range of activity. One of its most important functions is the international exchange service, and the map of the world here introduced, which shows the distribution of its correspondents, sets forth in a very telling manner the perfection to which this system has been carried. Not only are correspondents very numerous in the well-known countries, but we find, for example, 99 in China, 204 in Brazil, 24 in Iceland, etc. The total number of correspondents is very nearly 30,000.

Much of interest is given in regard to the workings of the Smithsonian in every direction, but we can only speak particularly of the Astrophysical Observatory. Mr. C. G. Abbott, in charge, enumerates as follows the most important features of the work of the past year:

1. The instrumental equipment has received valuable accessions, including a highly sensitive galvanometer, designed and constructed at the Observatory; two cylindric mirrors by Brashear (which, as used for collimation of the spectroscope, are equivalent to a lens of 64 meters focal length), and, finally and most important of all, a system of cooling by the expansion of ammonia, which has made possible an extension of constant temperature conditions to cover the five months of March, April, May, September, and October, otherwise frequently too warm. At present the change of temperature of the inner room between these warmer and the coldest winter months is only a fraction of a degree centigrade, and during an hour's observation it is generally less than one-tenth degree, the control being automatic.

2. Many bolographs of the infra-red solar spectrum have been taken, which, in consequence of these improvements, have yielded results threefold richer in "real" detail corresponding to solar and telluric absorption lines than any hitherto obtained.

3. About 40 of these bolographs have been compared, as described in the Appendix to the Secretary's Report for 1896, and 21 of the most perfect have been measured upon the comparator to determine the positions of the deflections found to be "real," or, in other words, corresponding to either solar or telluric absorption lines. These comparator measurements included about 44,000 separate observations.

There have thus been found over 700 absorption lines in the infra-red solar spectrum between wave-lengths 0.76  $\mu$  and 6.0  $\mu$ , an increase of about 500 over last year's results.

4. With the purpose of making a more accurate determination of the wave-lengths corresponding to the well-determined positions of the absorption lines discovered in the rock-salt prismatic spectrum, a very exact comparison of the dispersion of rock salt and fluorite has been made. This comparison will allow the indirect employment of certain recent and apparently very accurate determinations of the wave-lengths in the fluorite prismatic spectrum. Apparatus has been made ready and certain preliminary observations have been taken to directly measure the dispersion of rock salt. It is hoped that these steps will result in furnishing the wave-lengths of the infra-red absorption lines to a degree of accuracy corresponding to the exactness of the determination of their prismatic deviations.

5. Many interesting instances of local variations in the absorption have been noticed. Among these by far the most striking is a great decrease in the absorption at the longer wave-length side of the great band  $\psi$  at about 1.4  $\mu$ . This change occurred about February 15, 1898, and caused the bolographs to take on quite a different form at the place in question. This new form continued through the months of March and April, but in the month of May the usual form was gradually restored. It is found, by reference to former bolographs, that this marked decrease in absorption at this point takes place annually at about the same period, which coincides (fortuitously or otherwise) very nearly with that at which there is the greatest activity of growth in the vegetable kingdom. This raises the question whether the growth of vegetation does not abstract from the air great quantities of some selectively absorbing vapor active in absorption at this wavelength.

Whether such be the case or not future investigation must

determine, but enough variations in the absorption have been observed to indicate that the Observatory is now in condition to make advances along the line indicated in the Secretary's Report for 1892, in which is pointed out the important relations of astrophysics to meteorology.

2. Physical Geography ; by WILLIAM MORRIS DAVIS; pp. xviii, 428, with nine plates, etc. Boston, 1899 (Ginn & Co.).— This volume has the necessary elements of a high grade textbook: it is scientifically accurate, contains no unnecessary matter and is written in a pleasing manner. The earth's features are not only described, they are explained, and the reader is led to see a rational meaning in the varied land-forms about him. The student is constantly reminded, also, of the way in which physical features and climate have influenced man in his settlements, industries and manner of life.

The illustrations deserve special praise both in their selection and mechanical execution. The numerous "block-diagrams" are particularly valuable. Education in general and the out-of-door sciences in particular will be benefited by the introduction of just such text-books into secondary schools.

3. The Annual Report of the Director of the Field Columbian Museum to the Board of Trustees, for 1897-98. Report Series, Volume I, No. 4. Chicago, October, 1898.—This Report gives an interesting summary of the work of the Field Columbian Museum for 1897 and 1898. The numerous illustrations introduced give views of many of the rooms with their collections, and also of some of the objects of particular importance.

#### OBITUARY.

Prof. LOUIS W. PECK, for several years of the department of Physics in the University of Minnesota, died in Tucson, Arizona, on December 26th, in the 47th year of his age. He was born in Providence, R. I., and was educated in the Mass. Institute of Technology. He also served an apprenticeship in the Harris Corliss Engine Works in Providence. Prof. Peck's contributions to science were made in the investigation of the flouring mill explosion that occurred in Minneapolis, Minn., May 2, 1878. The mills exploded and then burned. They were insured against loss by fire and it became a question of great importance whether fire caused the explosion or the explosion caused the fire. Prof. Peck contrived a simple apparatus by which he showed that flour and wheat dust, when mixed with air in suitable proportions, would explode with terrific force if ignited with flame. Glowing charcoal and white hot platinum wires would not ignite the mixture, hence the conclusion was inevitable, confirmed by collateral evidence, that the mills were on fire before they exploded. Prof. Peck's results were embodied in a paper which was published in the Popular Science Monthly, xiv, p. 159, and the London Journal of Science, xvi, p. 666. This paper was widely copied and reviewed. S. F. P.

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WITH PLATES VI-VII.

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#### ΤΗΕ

## AMERICAN JOURNAL OF SCIENCE

#### [FOURTH SERIES.]

#### ART. XXV.—Glacial Lakes Newberry, Warren and Dana, in Central New York; by H. L. FAIRCHILD. (With Plate VI.)

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#### Introduction.

THE ice sheet of the last glacial epoch covered, during its greatest extent, all the area of the Great Lakes. When the receding front of the waning glacier had passed to northward of the southern boundary of the Laurentian basin, the glacial and meteoric waters were impounded between the ice front and the north-sloping land surface. These glacial lakes had their outlets southward across the divide, and they expanded northward as the barrier of ice receded. The local lakes were gradually united by draining of higher levels to lower, and ultimately these glacial waters became of vast extent, exceeding in breadth and depth any existing lakes. Their shorelines have been found at many localities and traced for great distances and the romantic history and relationship of the glacial waters have become in recent years the subject of a special body of earth-science literature.

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#### 250 H. L. Fairchild-Glacial Lakes in Central New York.

During the later phase of the Laurentian glacial waters, Lake Warren invaded central New York from the west, and drew down to its level the local waters of the Finger Lakes valleys. This region is of special interest, on account of its singular topographic character, and because it includes the critical locality where the great Warren waters found lower escape to the sea (than by the westward outlet to the Mississippi) and excavated in their flow toward the Mohawk a series of remarkable channels, piling the debris in great deltas in the more quiet waters of the intersected valleys.

The abandoned rock channels and correlating deltas are the most conspicuous features produced by the glacial waters. Southeast of Syracuse these great cuts in rock, some of them headed by cataracts, lie so close together that they cannot be represented satisfactorily upon the map (Plate VI). They are the last records of a lake history of truly dramatic interest. Their examination will repay not only the special student in geology and physiography, but the person having merely a general or casual interest in those sciences.

The study of the glacial lake phenomena in New York State has now been carried so far that the principal facts and relations in the history of those waters are known. It is the purpose of this writing to describe briefly the succession of events in the life and extinction of the later and broader glacial waters in the critical district of the Finger Lakes.

#### Description of the Maps, p. 251 and Plate VI.

The larger map locates in a generalized way the shorelines of the four greater glacial lakes, Newberry, Warren, Dana, and Iroquois.

The outlet of Lake Newberry was south to the Chemung River through the col (900 feet altitude) at the head of the Seneca Valley. The probable eastward limit of this water is indicated between Cayuga and Owasco Valleys, and the locality of its destructive drainage or lowering into Lake Warren is shown east of the north end of Canandaigua Lake.

The Warren waters found their first eastward escape southeast of Syracuse by either the channel west of Butternut Valley, with altitude 840 feet, or the one east of that valley with elevation 890 feet. (The channels are better shown on the smaller map.) The uncertainty as to the earliest spillway is indicated by the broken termination of the eastern end of the Warren shoreline. The most westerly of the hypo-Warren outlets is the one north of Skaneateles with elevation 812 feet. East of this channel is a series of channels which conveyed the overflow eastward to lower and lower levels.



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Lake Dana is a stage of the waters having their level determined by the outlet channel east of Marcellus, elevation 691 feet, with which the Dana shoreline terminates.

The several rock channels cut by the east-flowing waters in their escape to the Mohawk-Hudson lie so near together that they cannot be well represented on the larger map (Plate VI), but they are more clearly shown on the smaller map, p. 251.

The small circles on the larger map indicate cities or villages, the names of which are omitted to save confusion. On the smaller map the names are given.

The heavy broken line indicates the post-glacial divide between Laurentian and south-flowing waters. Bars drawn transverse to the water-parting indicate the location of outlets of the primitive local glacial lakes; those elsewhere on the map represent later outlets of secondary waters.

Numerals give elevations, in feet, above ocean level.

#### Physiography of the District.

The territory in general which includes the glacial lake phenomena described in this paper is that part of New York State known as the region of the "Finger" Lakes. Its more precise limitations are, on the west, the valley of Honeoye Lake and on the east a line somewhat beyond Syracuse. Those north and south valleys lying to the west of Honeoye, namely, Canadice, Conesus and the Genesee, were never related to the Newberry waters.

The accompanying map shows the hydrography of the present time. The topography will be sufficiently described, with the help of elevations given on the map, by stating that the area between Lake Ontario and the northern ends of the Finger Lakes is a plain of 400 to 600 feet elevation, while the north and south "Finger" Lake and intermediate valleys are preglacial trenches in an elevated tract of more enduring rocks. As far as the waning ice sheet upon the north left the land exposed, the northern and lower plain was covered by the Warren and Dana waters, which extended southward in a series of deep narrow bays up the valleys into the higher plateau. To the work of these lakes, with the subsequent Iroquois, is due the heavy silt deposits and the subdued topography of the lower part of this plain.

The ice movement, in the closing phase, followed the direction of the lake valleys, thus having a radial or spreading flow; and local lobes of the ice, or stream glaciers, protruded beyond the general ice front up each of the valleys, leaving in each valley a heavy moraine, which now constitutes the head of the present drainage, or the divide between north and south flow.

#### H. L. Fairchild-Glacial Lakes in Central New York. 253

The ice was probably thicker in the deeper and broader valleys of Seneca and Cayuga, and the general direction of the retreating front of the great ice body was probably convex toward the south, and for our theoretical discussion may be regarded as normal to the axes of the divergent valleys.

Since the glacial lakes were drained the beaches have been thrown out of horizontal position by a differential northward uplift that has affected the entire Laurentian area. It is therefore evident that during the life of the glacial lakes the altitude of Central New York was much less than now, and that the depression was progressively greater toward the north or somewhat east of north.

#### Earlier Local Glacial Lakes.

As the front of the ice sheet melted back upon the north of the divide, the larger valleys in Central New York were occupied by important local lakes, which had their overflow across the divide into southern drainage. These lakes have been described with some detail in former papers by the writer.\* For the present purpose it will be sufficient to enumerate the lakes and briefly state their location and relationship.

The glacial Honeoye occupied the valley of that name and sent its overflow into the Canandaigua Valley. At an earlier time the Honeoye Valley was flooded by the Canandaigua waters (Naples Lake).

The Naples Lake was the earliest glacial water in the Canandaigua Valley, with its outlet across the divide at the head of the valley, near Atlanta station. Subsequently a lower escape was found across the eastern border of the basin into the Flint Creek Valley and the, waters became tributary to those in the Keuka Valley (Hammondsport Lake). This later phase of the Canandaigua waters is called the Naples-Middlesex Lake.

The Italy Lake occupied the upper Flint Creek Valley and overflowed at the head of the valley into Naples Lake. A lower stage of Flint Creek Valley waters, the Potter Lake, has not been fully studied at the time of this writing.

The Hammondsport Lake occupied the Keuka Valley. This valley had a lake history similar to that of the Canandaigua. The early phase of the Hammondsport Lake had its outlet south through Bath village. A later phase had its outlet across the eastern rim through the village of Wayne, but ultimately to the Cohocton Creek, like the earlier phase.

<sup>\*</sup>Glacial Lakes of Western New York, Bull. Geol. Soc. Amer., vol. vi, p. 353; Genesee Glacial Lakes, ibid., vol. vii, p. 423; Lake Warren Shorelines in Western New York and the Geneva Beach, ibid., vol. vii, p. 269; Glacial Waters in the Finger Lakes Region of New York, ibid., vol. x, p. 27-68.

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The Watkins Lake occupied the upper Seneca Valley with outlet at Horseheads to the Chemung River. This was the predecessor of Lake Newberry, the latter being simply the former lake widely expanded into the Cayuga and other valleys adjacent to the Seneca Valley. (See page 255).

The Ithaca Lake occupied the Cayuga Valley with an outlet southeast to Catatonk Creek and the Susquehanna River.

The Groton and Moravia Lakes occupied the Owasco Valley, the former being the primitive lake in the main valley with outlet at Freeville, the latter being the later and larger lake with lower outlet southwest; both stages being tributary to the Caynga waters.

The first glacial Skaneateles, in the valley of that name, overflowed by the head of the valley past Scott village and Homer to the Tioughnioga Creek, but a later and much lower stage, called the Mandana Lake (from the name of its outlet) received the overflow of glacial waters of the Otisco and Onondaga Valleys, and had its outlet westward into the Warren waters, which then occupied the Owasco Valley.

The glacial Otisco overflowed at first southward past Preble village to the Tioughnioga Creek, but a later stage of the waters, the Marietta Lake, had outlet westward into the lower stage of the Skaneateles. At the foot of this valley, and also of the Onondaga and Butternut Valleys, we find the great channels and deltas, produced by the eastward flow of Warren and later waters, which are to be discussed in this paper.

The Cardiff Lake occupied the upper Onondaga Valley and overflowed through the site of the Tully Lakes to the Tioughnioga Creek. A later, lower lake in the middle section of the Onondaga, the south Onondaga Lake, had its outlet by two successive channels westward to the Marietta Lake in the Otisco Valley.

Butternut Valley was long occupied by a primitive glacial lake, called the Butternut Lake, with outlet near Apulia station to the Tioughnioga Creek below Tully village. When the valley was nearly clear of ice the glacial waters escaped for a time westward into the Onondaga Valley.

Eastward is still another north and south valley involved in this history, that of Limestone Creek. The earlier local lake phenomena have not been studied, but the lower (northward) part of the valley was occupied by the hyper-Iroquois waters and related to the great eastward-leading river channels.

In the eastern valleys, Skaneateles, Otisco, and Onondaga, the later glacial lake history is intricate and with surprising changes of drainage. It will be noted that the later, local glacial waters drained westward—those of the Butternut Valley into the Onondaga, the Onondaga into the Otisco, the latter into the Skaneateles and this into the Owasco Valley, then occupied by the great Lake Warren. The westward-leading channels of these earlier waters are shown on page 251. When, however, Lake Warren found eastward escape, all these valleys were drained eastward with the lowering Warren or hyper-Iroquois waters.

#### Lake Newberry.

Origin.—The lowest of all the cols across the line of waterparting separating the present north and south drainage in New York is the one at Horseheads, the head of the Seneca Valley, with elevation of 900 feet. This great channel\* is the final result of the erosion by the concentrated glacial drainage from the district lying between and including Honeoye Valley on the west and Owasco Valley on the east. Originally the channel carried only the overflow of the Watkins Lake and was doubtless somewhat higher than now, but the amount of the down-cutting has not been determined. The name "Watkins" lake applies to the waters as long as they were limited to the Seneca Valley. Lake Newberry may be regarded as having its birth when, by the recession of the ice front, the waters of either the Ithaca or the Hammondsport Lake were drained down to and became confluent with the Seneca Valley waters. Lake Newberry is therefore only the larger, more expanded Watkins Lake. The former name is used, not only as a matter of convenience but also for uniformity in glacial lake nomenclature; in order to distinguish the broad waters with complex relationship from the smaller, more localized, and simpler Watkins Lake.

Judging from the topography of the region, it seems more probable that the first local lake to lose itself in the Horseheads level was the Hammondsport. The locality of its overflow was probably near 2d Milo, four miles south of Penn Yan.

Extent and tributaries.—Upon the west, Keuka Valley became a gulf of the Newberry waters, first by the Penn Yan depression and later by the open valley to the north. Flint Creek Valley became a bay of the greater lake when the ice receded from the locality of Stanley and Gorham. The waters of Canandaigua and Honeove Valleys were certainly tributary to the Hammondsport Lake through the Flint Valley, and probably continued tributary to the Flint Valley waters even after they were a part of Lake Newberry.

Upon the east, the Ithaca Lake found its close when the ice withdrew as far north as Ovid. The scourways made by the escaping Ithaca waters show an east and west erosion of the

\*The Horseheads channel is described and figured in a former paper, Bull. Geol. Soc. Amer., vol. vi, p. 365.

drumlin surface in and south of Ovid village. In the Caynga Valley the Newberry waters existed for a time sufficient to produce clear evidences of its presence, but as to Owasco Valley the evidence is negative. They may have existed there a short time, or the ice dam toward the Canandaigua V-alley may have lifted and drained Lake Newberry before the removal of that which barred the Owasco waters. The earlier Owasco waters (Moravia Lake) were certainly tributary to Lake Newberry by the North Lansing-Ludlowville channel and probably were the easternmost of such tributary waters.

Lake Newberry certainly included the valleys of Flint Creek, Keuka, Seneca, and Cayuga Lakes, and possibly Owasco for a brief time. In form the lake was an east and west belt of water resting against the ice front, and with four deep bays reaching southward up the valleys above named. Its linear extent was considerable, and its shoreline great, but its total area was not large in proportion.

Shorelines and Elevations.—The phenomena of the Newberry shorelines have been observed, chiefly as terraces, and wave-built bars on terraces, of landstream deltas, throughout the Keuka and Seneca Valleys and in the southern part of the Cayuga Valley. These have all been described in detail in another writing\* and it will be sufficient here to briefly mention the localities and altitudes.

In the Seneca Valley the Newberry shore phenomena have been measured at many localities; at the head of the valley between Odessa and Montour Falls (Havana), 935 to 940 feet; at Montour Falls, 950 feet (aneroid). On the west side, at Watkins, 960 feet; at Himrods, 990 (?) feet (aneroid); at Stanley 970 feet. Between Reed's Corners and Ennerdale occur the channels which drained the lake to the Warren level, 985 feet to 930 feet (aneroid). On the east side of the valley are good delta ridges at Burdett, 964 feet; at Heetor's Station, 976 feet; at North Hector Station, 984 feet; at Lodi, 977 feet. At Ovid the level is in the village, but the exact elevation is undetermined.

In the Cayuga Valley well-defined beach ridges occur at Trumansburg, 962 feet elevation. No effort has been made to locate the shore phenomena at other points, but they can undoubtedly be found throughout the valley.

In Keuka Valley the main delta terraces throughout the valley are 955 to 970 feet elevation, and are attributed to Newberry waters.

The northward rise of these altitudes is evident and measurable, but the matter of beach deformation will not be discussed in this paper.

\*Glacial Waters in the Finger Lakes Region of New York, Bull. Geol. Soc. Amer., vol. x, p. 27-68.
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Extinction .--- In the study of the glacial lake history, it was recognized that Lake Newberry must have been destroyed by outflow either to the east or west, eastward by the Mohawk Valley, or westward into Lake Warren. It was a matter of the quicker removal of the ice barrier in one or the other of two critical localities. And wherever the escape occurred we should find the scourways across the north-sloping land, or some transverse configuration with traces of erosion by the escaping waters, and with a favoring relation of valleys or openings beyond. With some knowledge of the topography of the critical east and west localities and their general conditions and relations, it was thought more probable that the Newberry waters escaped westward, and an examination of the eastern area at the foot of Skaneateles and Otisco Valleys, supplemented by a study of the Skaneateles sheet (unpublished) of the New York topographic map, confirms this view of the Newberry extinction. The writer has found no evidences of water at the Newberry level in the Skaneateles Valley, but such should occur if the waters found egress eastward, because the low Mandana pass (900 feet), east side of the middle of the valley, would have let in the waters long before the ice dam was removed from the high ground northeast of the valley. Indeed no conclusive evidence has been found of Newberry waters in the Owasco Valley, west of the Skaneateles. Moreover, the channel cut by the eastward escape of the subsequent and lower Warren waters lies only a few miles north of the high ground at the north end of Skaneateles Valley, and within this short distance of critical ground there are no east and west scourways or any evidence of water-flow between the Newberry and the Warren levels.

Lake Newberry was destroyed by draining westward over a point of land about five miles southeast of Canandaigua village, and midway between Ennerdale railroad station and Reed's Corners (see Plate VI). Here are well-defined and capacious channels, at successively lower levels, lying athwart the icemoulded or drumlin surface. They occur on the south side of a morainal series and truncate the ends of drumlins. Here the Newberry waters were lowered to the Warren level, being drained from about 980 feet elevation down to 880 feet, and at the lower level the waters of the former Newberry area became a part of the great Lake Warren.

## Lake Warren.

General Description.\*—This glacial lake was of great area. It is believed to have covered at least the southern part of the Huron basin, all of the Erie basin, and as much of the Ontario

\* A fuller description will be found in Bull. Geol. Soc. Amer., vol. viii, p. 269.

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basin as was not still buried under the great ice-body. The beaches have been traced in the Huron-Erie basin and along the southern slope of the Erie and Ontario basins into Western New York as far east as the meridian of Rochester. The outlet of the lake was certainly westward into Mississippi drainage, probably across Michigan into the glacial lake Chicago. The name was given by J. W. Spencer.

Invasion of Central New York. — The Warren waters existed in the extreme western part of the state, within the Erie basin, for a long time before they were allowed to enter the central part of the state. When the front of the ice barrier moved back, northward, from the high ground north of Batavia, Lake Warren extended eastward, as a relatively narrow belt of water, along the east and west ice-wall, with southward prolongations in the valleys. The waters occupied the valley of Oatka Creek to beyond Warsaw; of the Genesee and Canaseraga Valleys to beyond Dansville; the valley of Conesus, and ultimately the valleys of Honeoye, Mud Creek (Bristol), Canandaigua, Flint Creek, Seneca, Keuka (through Seneca). Cayuga, Owasco, Skaneateles, Otisco, Onondaga, and possibly Butternut. The valleys of Hemlock and Canadice were above the Warren level.

The breadth and southward extent of Warren waters in the valleys of Keuka, Seneca, and Cayuga were less than that of the Newberry waters, as they were about 100 feet lower. The northern boundary, the ice front, was probably much straighter or less lobate than that of Newberry. The glacial border being further north, on the low northern plain, the effect of the Finger Lakes valleys was nearly or entirely lost upon the ice-front, which was probably an arcuate line not far from the north ends of the present lakes.

Shorelines and Elevations.—The Warren shore has been traced with sufficient continuity to positively identify it as far east as Lima, south of Rochester, where it has an elevation of 879 feet. Well-defined beaches may doubtless be found further east, but the shoreline phenomena already discovered are delta terraces and bars and spits connected with deltas. Like the Newberry phenomena, these have been elsewhere described and need only be mentioned here.

In the Canandaigua Valley the Warren level appears upon the deltas, but the elevations have not been measured. A fragment of beach has been found southeast of Canandaigua village and one mile west of Reeds corners with elevation of about 880 feet. In the Keuka Valley the Warren level is very evident as the lowest of the strong delta terraces. These vary in elevation from 830 to 870 feet. In the Seneca Valley several terrace bars have been measured as follows: At Montour Falls, 840 feet; between Montour Falls and Odessa, 840 feet; at Himrods, 853 feet (?); at Hector Station, 872 feet; at Lodi Station, 874 feet; at Ovid, 877 feet.\*

In the Cayuga Valley the Warren levels have been measured at Coy Glen, 831 feet, with a higher bench 865 feet; at Willow Creek, 829 to 863 feet; at Taughannock Falls, 826 to 849 feet; at Trumansburg, 829 to 834 feet. In the Owasco Valley, at Locke, 860 to 870 feet, and at Moravia, 855 to 882 feet (aneroid). The two levels in the Cayuga and Owasco Valleys are significant. These vary from 23 to 34 feet apart and are thought to represent the fall from the normal Warren level down to the first enduring level with eastward discharge, possibly the rock sill at the head of the channel southeast of Jamesville (see pages 251 and 260). The lower level is hypo-Warren, or, more accurately, hyper-Iroquois.

Extinction.—The life of Lake Warren was terminated by the opening of a new and lower outlet, eastward, past the icefront, to the Mohawk-Hudson. For a long period, perhaps several thousand years, its waters had been tributary to the Mississippi, but for some centuries they had been creeping eastward along the ice front as if in patient search for a new escape that was sure to come. It should be kept in mind that the district we are considering has been uplifted to its present level since that time; it then lay at a much lower altitude.

The most western spillway of the eastern discharge of Warren waters is on the crest of the Corniferous escarpment four miles west northwest of Marcellus village, and the same distance north-northeast of Skaneateles. The present elevation of the sill or intake at the lowest point is given by Mr. Gilbert as 812 feet, which is perhaps 80 or 90 feet under the theoretical Warren plane. There has been some removal of overlying drift and possibly of shale, and the intake has probably migrated backward to the present point. But this outlet, the "Gulf," was probably not the earliest nor highest spillway. In another writing (see reference, p. 256) reasons have been given for believing that the Warren waters at their full height invaded the region as far east as the Onondaga Valley and possibly the Butternut Valley. Their first and highest eastern escape was east of the Onondaga Valley, in the vicinity of Jamesville (see map, p. 251) and the waters were quietly lowered upon the hollows between drumlins at the head of the Gulf channel.

For years after the eastern escape was opened Lake Warren must have had two outlets and divided its contribution of surplus water between the Atlantic and the Gulf of Mexico; but soon after the Gulf outlet was opened it doubtless carried the entire overflow. Whenever this occurred the lake was no longer Lake Warren.

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This large channel, excavated in Hamilton shales by the Warren overflow, leads southeast four miles, opening into the Otisco Valley two miles south of Marcellus village. The local name is the "Gulf," which, for want of a better name is retained. The waters were again impounded in the Otisco Valley, where the debris derived from the excavation of the Gulf was piled in a delta, with terraces from 860 down to 800 feet elevation. The Otisco waters (Marcellus Lake) escaped by another great rock channel, Cedarvale channel (named after a hamlet in the gorge) that heads at Marcellus village and leads southeast to the Onondaga Valley at South Onondaga.

These great channels, with others farther east (see page 251), show the final result of some centuries of erosion. Their initiation was probably not in the present geographic sequence, and the primitive conditions of elevation, etc., are uncertain. The Skaneateles and Tully sheets of the New York State topographic map will, when published, show the Gulf and Cedarvale channels and deltas with clearness.\* Dr. Gilbert was the first to study these channels and to point out their relationship to those lying further east.+

## Hyper-Iroquois Waters.

Lake Dana ("Geneva" beach).-At the time of Warren extinction the Ontario basin was still largely occupied by the glacier. Certainly most of the eastern part of the basin north of the locality now under discussion was filled with the ice. Considerable time was required for the front of this ice-body to recede so far as to permit an expanse of Ontario waters in the region under discussion, with immediate outlet at Romethat is to say, for the westward expansion of Lake Iroquois. During this interval the glacial waters fell about 500 feet, from the Warren plane to the Iroquois. This subsidence was not a steady or continuous lowering, but per saltum,-a series of comparatively sudden falls, as progressively lower outlets were opened, with intervals of steady level, or very slow falling, as each outlet remained effective.

During one of these phases of repose it is believed that the beach was formed which has been traced along the west side of the Seneca Valley and described in a former paper as the "Geneva" beach.<sup>‡</sup> It is also believed that the level of the beach correlates with the Cedarvale outlet at Marcellus. This is the only waterlevel between the Warren and Iroquois planes

\*To the U.S. Geological Survey the writer is indebted for advance copies of the maps in manuscript which have facilitated this study. † Old Tracks of Erian Drainage in Western New York, by G. K. Gilbert. Bull.

Geol. Soc. Amer., vol. viii, p. 285.

‡ Bull. Geol. Soc. Amer., vol. viii, p. 281; vol. x, p. 44.

that has left any strong shoreline phenomena, so far as at present observed. Theoretically its evidences should be found from Marcellus westward throughout the Ontario and Erie basins, and it may be the subject of much future study. A distinctive name is required, and it is proposed to call the water Lake Dana, after Professor James D. Dana, the early leader in American glacial geology.

Since the publication of the former description the beach has been traced south from Geneva to near Dresden, and shoreline phenomena have been observed in the Cayuga Valley at a theoretically corresponding level. The elevations in the Seneca Valley are as follows: near Angus station, Fall Brook railroad, 671 feet; near Earle's station, 679 feet; west of Geneva, 700 feet; south of Phelps, 713 feet. The deformation of the beach is about three feet per mile, on north and south line, and it lies  $180 \pm$  feet under the Warren plane. Evidences of this lake should be found throughout the valleys of Cayuga and Seneca and westward at 170 to 190 feet under the Warren level. This water could not occupy the valleys of Keuka, Owasco, Skaneateles, nor Otisco, as these lie above its plane.

The magnificent Cedarvale channel, with its huge delta, has been described in another writing (see reference, p. 256). It heads on Corniferous limestone and shale, one-fourth mile southeast of Marcellus village, with an average elevation of 691 feet, which elevation correlates well with the beach altitude of the same parallel, something over 700 feet, making allowance for depth of water over the sill and the later downcutting, with some east and west deformation of the land.

The change from the Warren level to the Dana level did not come by the slow down-cutting of the head of the Gulf channel, but by the recession of the ice front so that the glacial waters abandoned that outlet and found free access to the Marcellus valley from the north.

The eastern limit of Lake Dana was practically the same as that of Lake Warren, but with a surface  $180 \pm$  feet lower. Its southern margin must have been more contracted, while the ice boundary upon the north was somewhat further removed. Its western limits have not been determined, but phenomena attributed to this water have been observed as far west as the Genesee River. Without some unexpected barrier, like great land elevation or far readvance of the ice sheet, there seems no escape from the conclusion that Lake Dana must have covered the Erie basin. Being weak as compared with the Warren phenomena, these have been overlooked, but it is predicted that they will be found westward over a wide area. The hypothetical shoreline is indicated on the map.

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Water levels between Lakes Dana and Iroquois .- In the district south and east of Syracuse there are several other abandoned channels. All are lower than those described above; some of them are in rock and of great capacity. The most interesting ones are the sluiceways which carried east-ward the overflow of Warren and Dana Lakes, and which constitute, with the Gulf and Cedarvale channels, a connected series (see page 251). All this series lie transverse to the present drainage and conveyed eastward, across the intervening high lands, the waters impounded by the ice-dam in the north and south valleys. The flood poured into the Onondaga Valley from the hypo-Warren and Dana Lakes by the Cedarvale channel was carried over to the Butternut Valley by three successive channels lying southeast of Syracuse and near Jamesville. The lowest and most important is a great "rock cut," three miles southeast of Syracuse. While perhaps not the largest, this channel is the finest, the most typical, and the most easily seen of any glacial channel in New York. It is about three miles long and is traversed, its whole length, by the Delaware, Lackawanna & Western railroad, and has been named the "Railroad" channel. The walls are nearly vertical bare rock, 125 to 150 feet high, and the bottom of the cut will average 900 feet wide.

The water was conveyed eastward from the Butternut Valley to the Limestone Valley by other great rock channels, the largest and latest one heading opposite the mouth of the Railroad channel and extending somewhat over three miles to High Bridge, south of Fayetteville. The Syracuse sheet of the topographic map well portrays the Railroad channel, but the High Bridge channel is not well delineated on the north side by the 20-feet contours. From the valley of Limestone Creek three channels lead northeast; the highest of these heads in a cataract, one and one-half miles southwest of Mycenae, and joins the second channel, which ends at Mycenae above the Iroquois level. The lower waterway holds Round and Green Lakes, which occupy depressions produced, as pointed out by Dr. Gilbert, by the sinking of strata due to solution of the underlying salt beds. The heads of these three channels are higher than the High Bridge channel, and they probably ceased to be effective earlier. Indeed they were probably the first of the east and west series to be abandoned, excepting the 890 feet ("Green's") channel, south of High Bridge.

Northward of the outlet series described above, lies another, later, series of channels. The Syracuse sheet exhibits a broad channel, heading a mile east of Fairmount at 500 feet elevation, which passes eastward directly through the center of Syracuse, where its elevation is only 400 feet. West of Syra-

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cuse they have not been mapped, but another and lower watercourse may be seen from the Auburn branch of the New York Central railroad, heading in a cataract west of Marcellus station and followed by the railroad eastward to beyond Camillus.

It is possible that one or more of the channels lower in elevation than the Cedarvale channel may have established for a short time an independent lake level, but such waters could not have extended westward beyond the Ontario basin, as the planes of these outlets are below that of Niagara.

Upon the north sides of these channels the morainal drift is heavy and the topography more irregular than shown by the topographic sheets.

### Lake Iroquois.

These latest glacial waters of the Ontario basin have been so long known that extended description is unnecessary here. The name was given by J. W. Spencer, and Mr. Gilbert correlated the shorelines with the col and ancient outlet at Rome. This large and important body of water had a long life, during which it matured its western shorelines and expanded to an area larger than that of the present Ontario, as its surface was far higher than Ontario, although the retreating ice barrier during most of the life of Iroquois held possession of some of the northern or northeastern part of the basin.

During the life of Iroquois the differential elevation toward the north-northwest, or canting of the basin toward the southsouthwest, produced a shifting of the shorelines, a transgression of the waters upon the southern shores and a recession from the northern shores. This has been graphically shown by Dr. Gilbert.\*

The Iroquois shoreline was not matured east of Sodus although abundant evidence of the water action exists. South and east of Sodus Bay the map gives only the general or hypothetical position of the water line.

The lake became extinct by the opening of the St. Lawrence Valley and lowering of the water below the Rome outlet. At this time the altitude of the basin was such that the head of the St. Lawrence channel, at the Thousand Islands, was below sea-level, and a gulf of the ocean occupied the Ontario basin. The differential uplift, however, soon barred the sea and initiated the present lake and river.

\*"The History of the Niagara River," 6th Ann. Rept. Com. of State Res. of Niagara, Albany, 1890.

## ART. XXVI.—A Rapid Method for the Determination of the Amount of Soluble Mineral Matter in a Soil; by THOS. H. MEANS.

A RAPID and simple method for the determination of the per cent of soluble matter which a soil contains has been found very desirable where areas of soil are to be studied in any detail. Particularly is this true in the arid and semi-arid regions of the West where accumulations of soluble salts have been the cause of injury to valuable tracts of land. The ordinary methods of chemical analysis are entirely too laborious for the examination of a large number of samples, and, besides, chemical analyses cannot be made out in the field. In field studies it is of great advantage to know the salt-content of the soil at hand. The accumulation of "alkali," wherever irrigation has been practiced a few years, has pointed out the great necessity of studying the conditions of the soluble matter before water is applied. Enormous sums of money are being invested in irrigation, and a great deal of this expended capital has been, or will be, lost unless new systems of irrigation and drainage are devised. There can be no question that the study of the soil, the alkali and the methods for the prevention of its accumulation, must form an integral part of every irrigation engineering problem. Not only must the surface of the soil be examined, but the per cent of salt found in the subsoil to a depth of 30 or 40 feet should be known. In order that underground maps of the salt may be prepared with much greater ease than is possible with ordinary means, the following method is suggested.

The electrical conductivity of water varies with the amount of dissociated salt that is present. The method is practically a means of determining the specific electrical conductivity (or resistance) of the solution between the soil grains. When this is known, the amount of any salt which will produce this same conductivity may be calculated from published tables of the conductivity of salt solutions.\*

In order to determine the effect of the solid grains of the soil upon the resistance of the solution, the following experiment was arranged. A hard rubber cell with parallel sides of metal was partly filled with a solution of known specific resistance. Then as much dry soil was added as would be taken up by the solution, forming a saturated soil. The resistance was in all cases increased. A correction was made for the soluble matter contained in the soil, and the increase in

\* Kohlrausch, Wied. Ann., 1879, vol. vi, p. 145.

resistance, due to the addition of the solid non-conducting particles, was therefore determined. In this way a large number of samples were examined and it was found that the increase in resistance was nearly the same for soils of very different textures. The following table contains the most important of the results:

Number of devermina- tions.	Soil and character.	Per cent water when saturated.*	Initial resistance. Ohms.	Resistance after soil is added. Ohms.	Factor of texture.
10	Loess, Virginia City, Ill. Silty	31.84	1	1.81	•551
30		35*36	1	1.73	•579
10	Limestone soil, Blacksburg, Va. Heavy clay	69.41	1	1.90	•527
10	11 · · · · · · · · · · · · · · · · · ·	72.49	1	1.85	$\cdot 542$
ō	Red Land, S. C. Clay soil	49 00	1	1.83	.557
õ		36.35	1	1.88	·533
õ	,	32.75	1	1.93	•517
10	Sea Island, Cotton soil, S. C. Fine sand	25.77	1	1.83	·547
10	Early Truck soil, Md. Coarse sand	17.94	1	1.78	.563
	······			Average	•548

These soils, as seen in the table, vary from the light sandy lands, which require less than 18 per cent (of their dry weight) of water to saturate them, to the heaviest of clays, requiring 70 per cent of water for saturation. Determinations were made with two or three amounts of water in some of the soils in order to strike as near as possible the point of saturation. The last column is the ratio between the resistance after the soil was saturated and the initial resistance of the solution. If the resistance (between parallel electrodes) of a saturated soil is multiplied by this figure (the factor of texture), the resistance of the solution between the soil grains will be found.

The salt determination is performed in practice as follows:

1. Saturate the soil with distilled water. The point of saturation can very easily be found and, with a little practice, duplicate samples can be mixed to within a small error.

2. Pack saturated soil in a cubic cell with two sides of metal and take the resistance. Read the temperature, and correct resistance for temperature.<sup>†</sup> Multiply the corrected resistance by the factor of texture, 0.55. This gives the resistance of the soil solution alone in the cubic cell.

3. From the known weight of soil in the cell and the percentage of water required to saturate the soil, find the number of cubic centimeters of soil moisture between the soil grains. In field work it is sufficiently accurate to take the average of

\* Calculated on dry weight of soil.

+ Bulletin 7, Division of Soils, Department of Agriculture. Bulletin 8, Division of Soils, Department of Agriculture, page 27.

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several laboratory determinations of this quantity. The amount of soil moisture being known, the cell factor (the figure by which the resistance must be multiplied to obtain specific resistance) for this quantity can be found.\*

4. Multiply the resistance found in (2) by the cell factor and obtain the specific resistance of the soil solution. For dilute solutions the per cent of salt present is nearly inversely proportional to the resistance. In a study of the alkali soils of the West+ where the salts are of rather uniform chemical composition, it is of great advantage to have a more accurate method of calculating the results. In such studies, a solution of the average composition of the salts is made up and its resistance-salt curve determined. In this way the per cent of salt by weight can be reckoned for any resistance. Such a proceeding was followed in some studies of alkali soils in Montana.

This method offers special advantage in the study of alkali The apparatus necessary can readily be carried in the soils. field. A convenient form of Wheatstone's bridge adapted to field use has been designed by Mr. Lyman J. Briggs of this laboratory.

The auger for sampling the soil is in general use in the study of surface geology.§ The only other apparatus necessary are the cubic cell, thermometer, mixing dish and bottle of distilled water.

This method offers a ready means for the detailed study of irrigated districts. Two men can examine from sixty to one hundred samples of soil in a day and in this way cover considerable ground, obtaining sufficient data for the construction of salt maps of the district.

U. S. Department of Agriculture, Division of Soils.

\* Ostwald's Physico-Chemical Measurements, translated by Walker, page 225. Note.—If a cubical cell is used—such a cell  $4^{\circ m}$  internal dimensions has given me the best results-the cell factor will vary inversely as the number of cubic centimeters of solution present.

+ Whitney and Means, Bulletin 14, Division of Soils, Department of Agriculture. Loc. cit.

§ Darton, Am. Geol, vol. vii, page 117–119.
Whitney and Means, Bulletin 8, Division of Soils, Department of Agriculture, page 11.

# ART. XXVII.—On a New Type of Telescope Objective especially adapted for Spectroscopic Use; by CHARLES S. HASTINGS.

THE ordinary achromatic doublet as invented by Dolland in the last century, is, as is well known, very far from complying with the condition implied in its name. For telescopes of small aperture, or even for those of very considerable aperture, if a ratio of focal length to aperture as great as that customary with Dolland be employed, the defect in color correction is neither very conspicuous nor very harmful in ordinary But if the apertures are very large, as in our modern use. astronomical instruments, or if the length be reduced relatively to the diameter of the objective, this defect of secondary color aberration becomes very conspicuous and reduces the optical efficiency of the instrument very materially. The maximum inconvenience of the defect, however, falls upon the spectroscopist, who finds that, although the optical efficiency of his instrument is independent of the wave length of light which he happens to be observing, the instrumental adjustments must undergo frequent changes for adaptation to different portions of the spectrum. Another familiar and obvious consequence of the secondary color defect is the impracticability of adapting the same instrument to purposes of both eye and photographic observation.

It follows, therefore, that the solution of the problem, apparently first seriously undertaken by Fraunhofer, namely, to devise an absolutely color-free objective, is, and has long been, of continuously increasing moment. Fraunhofer failed; but unless I greatly misapprehend the meaning of his own record of his work, the effort led directly to the discovery of the Fraunhofer lines and to the beginning of spectroscopy. It is true that nowhere, as far as appears in his published writings, does he state that this was his aim; but in view of his very extended experiments in varying the constitution of his glasses, of his studies of the minute dispersion characteristics of various substances, and of the extraordinary skill and conscientiousness in perfecting an instrument which has possessed no other error of importance since his unequaled contributions to the art of telescope-making, few will question the validity of the inference.

Doubtless many investigators since Fraunhofer's time have attacked the same problem, but, so far as I am aware, without any recorded success until the writer showed, in a paper published in this Journal, vol. xviii, p. 429, that there were certain glasses, unfortunately not then procurable, which would yield

in a triple combination an objective entirely free from color. Since then the extraordinary increase in number of materials at the command of the optician, resulting from the labors of Dr. Schott of Jena, led the writer to return to the problem with the results which were published in a paper in vol. xxxvii of the same Journal, in 1889. A general method of dealing with all such problems was there developed and a number of triads were indicated which would yield the most favorable results. It is true that those given included a phosphate glass which was believed by the makers to be permanent and has since proved not to be so; but it was distinctly stated that the table exhibited a considerable number of other promising combinations, and the general method of recognizing them was pointed out.

It may properly be stated here that the latter paper also contained a general discussion of interesting double combinations, one of which promised to be of great value to spectroscopists; but the inability of glass makers to supply large disks of the materials in question proved an unforeseen difficulty. Still, the writer employed this construction for a number of years for his spectrometer and only displaced it recently by an improved type of objective. Professor Keeler has also employed the same construction, made by Mr. Brashear with my aid, satisfactorily in spectroscope work.

The experiments with triple combinations which followed the paper last named met with an unforeseen difficulty. The particular triad which promised most in theory proved to have in one of its members a perishable glass. This might possibly have been used by covering the objectionable material by a more permanent glass cemented to it, but this course is not without risk, and certain defects, to be noted later, are not so readily eliminated if this method be chosen. The only practicable course seemed to lie in replacing this material by one beyond suspicion, and much time was spent in investigating the possibilities of this meams. It was found, as appears from the paper cited above, that there was no difficulty in selecting triads which would meet the analytical condition, insuring complete elimination of color and subject to practical limitations as regards permanency; but the necessarily greater curvatures of the lens surfaces introduced a new source of imperfection, namely, chromatic difference of spherical aberration. Of course, this, like all other errors, is present to a greater or less degree in all optical instruments which depend in any way upon refraction for their action. In telescopes, however, this error has never been sufficiently great to betray itself to the users, although clearly indicated by theory. Gauss, indeed, a long time ago showed how to reduce this particular error to a

residual of a higher order of minuteness, but the fact that his construction has never come into use is a most convincing proof that the error is quite negligible as compared to other defects inherent in the ordinary construction. But when we try to make a color-free triple objective after the methods of the paper of 1889, we find that the defect in question becomes of great moment. Especially is this true if we prescribe the cementing of the objective so that there shall be only two free surfaces. Such an objective, if corrected as regards spherical aberration for light-waves of mean length, would have strong positive spherical aberration for the red and negative for the violet ends of the spectrum. It is true that this defect might not prove very obvious for a telescope which is to be used only for objects which are approximately white, but it would be intolerable in spectroscopic use. The obvious method of reducing the error is to increase the ratio of the focal length to the aperture. This method, however, would introduce such serious structural and mechanical difficulties, and so far reduce the convenience of handling all spectroscopes to which it might be applied, that it seemed to me quite impracticable.

As a possible means of securing the end in view, convinced as I am that its importance warrants any amount of labor, I lately turned to a consideration of the possibilities possessed by a combination of four varieties of glass. The investigation is necessarily somewhat laborious as appears from the unusual conditions imposed from the outset; but the time expended in attaining complete success was short compared to the protracted investigations which led to a definitive rejection of the triplet as quite inadequate. In short, I have constructed an objective, consisting of a quadruple combination of silicate flint, borosilicate flint, silicate crown and barium crown, which possesses all the properties demanded. It has but two free surfaces, the four lenses being cemented together. With an aperture of one-tenth the focal length, its focal plane is rigidly the same for all wave-lengths, from that of the Fraunhofer line A to that of K, while it is sensibly free from chromatic differences of magnification and of spherical aberration. With its perfect color correction, the well-known (but ordinarily overlooked) chromatic aberration of the eye becomes very sensible. This, however, I have eliminated by means of a specially devised ocular, so that in my instrument there is no reason why its length may not be made permanently invariable. One notable advantage in the construction will appear at once to all spectroscopists: wave-surfaces from the collimator being rigidly plane for all wave-lengths, the adjustment of the prisms for minimum deviation-provided always that their faces are accurately plane-ceases to be of importance. Thus a con-

struction, which must have occurred to every one who has seriously studied the theory of the spectroscope, in which the last prism of a train is of half the angle of the remainder and silvered on the back, so that the light retraces its course through the train, becomes entirely practical. Indeed, my experiments with the new telescope lead me to prefer a construction of spectroscope in which the collimator and telescope are set at constant angle, and the prisms, arranged as above, are alone movable. This is the familiar construction of the grating spectroscope.

Although the objective described above consists of four lenses, I imagine that a cemented system of five lenses would in some cases be preferable, especially in relatively large apertures; but there is no doubt in my mind that four kinds of glass are sufficient and, unless greater structural complexity is admitted, necessary for the ends defined.

Should the construction meet my confident expectation and supply the spectroscopist with an optical instrument combining the merits of a reflector with the greater merits of a refractor, it will be convenient to give it a characteristic name suggested by its properties. These are, as given above, chromatic differences of focal distance, of focal length, and of spherical aberration, all reduced to practically zero, together with a minimum possible number of free surfaces. As such an objective is the same in its action upon light of all wave-lengths, I propose to call it an *isokumatic* system.

Mr. Brashear of Allegheny, who made for me the prisms for the study of these glasses, as well as scores of others, and who has shown unfailing good nature and constant readiness to lend me his efficient aid in all my optical investigations, merits my unstinted acknowledgments. I have promised the necessary calculations if he is called upon to carry out for others this difficult piece of optical work which has yielded so much satisfaction to the writer.

Yale University, March, 1899.

## ART. XXVIII.—On the Phenocrysts of Intrusive Igneous Rocks;\* by L. V. PIRSSON.

THE igneous rocks, excluding those which have solidified as uncrystallized glasses, may be roughly divided into two classes, the granular, composed of mineral particles of approximately similar size, and the porphyritic, consisting of minerals exhibiting a more or less perfect outward crystal form which lie embedded in a so-called groundmass made up of much smaller, usually anhedral,<sup>†</sup> particles or even wholly or in part of glass. A rock belonging to this latter class is a porphyry and the larger embedded crystals are called "porphyritic crystals" or more conveniently "phenocrysts," a term proposed by Iddings which has obtained general recognition among geologists.

It is with respect to the origin of these phenocrysts in a certain class of igneous rocks that it is proposed to treat in this article.

Without going into details, it will be sufficient to recall that many petrographers have expressed the view that the phenoerysts of porphyritic rocks, by the very fact of their size, frequent perfection of crystal form and contrast of character to that of the groundmass in which they lie embedded, are older than this groundmass, have been formed under different physical and therefore different geological conditions, in short, not in the place where they now are, but at great depths, and hence they are frequently spoken of as "intratelluric" in origin.‡

The writer has been unable to find in the literature, that any sharp distinction has been drawn between the origin and character of the phenocrysts of *intrusive* igneous rocks and those of the *extrusive* ones or lava flows. This has probably arisen from the belief that phenocrysts are always formed, as stated above, at much greater depths than the place in which they are now found, and that therefore their origin is similar in both cases. It would thus make no difference in regard to their origin and character, whether the ascending magma which contained them was thrust in intrusive masses into the upper portion of the earth's crust or poured out on the surface in flows of lava.

In the present article, however, it is to be carefully noted that the writer confines himself to the phenocrysts of the *intrusive* rocks, as it is intended to show that not all phenocrysts are intratelluric in the sense that they have been formed at much greater depths than they now occur in, but that on the

<sup>\*</sup> Read before the Geological Society of America, December, 1898.

<sup>†</sup> i. e., having crystal structure but not crystal form.

<sup>&</sup>lt;sup>‡</sup> Rosenbusch, Mass. Gest., 3d ed., 1896, p. 553; Michel-Lévy, Struct. et Class. des Roches, 1889, p. 1 et seq. See also discussion by Zirkel, who does not follow this view, Lehrb. der Petrogr., 2d ed., 1893, vol. i, p. 737 et seq.

contrary in many cases they have been formed in place, and are of contemporaneous origin with the other constituents of the rocks, and the nature of the proofs is partly such that they can be applied only to intrusive rocks, and partly they have not been observed in lavas.

The idea that phenocrysts are not necessarily intratelluric has been expressed by previous writers, and Zirkel\* indeed gives a very full discussion of the subject, while Cross+ also mentions this belief in alluding to orthoclase phenocrysts which are found in certain laccoliths but not in the peripheral portions. But the subject does not appear to have received in general the attention that its importance merits, and the writer is therefore led to present his own observations bearing on this point, and the deductions he has drawn from them as a contribution to the subject. They have been gathered during the progress of the geological work in Montana, by Mr. W. H. Weed and the writer, and the details have mainly appeared in our publications on that region, but they are now gathered together and generalized for use upon this question. Similar proofs of course occur elsewhere, and they are indeed of general application.

Meaning of intratelluric.—The term "intratelluric" needs a moment's attention. It is probable that different writers have used it with somewhat different ideas, differing as to degree, not as to kind. Nowhere has the writer been able to find a precise definition by an author of what his idea of intratelluric is, but it is certain from the context, that in all cases, as regards *time* and *niveau*, it means an earlier period and greater depth of the magma than that in which it came to rest. Thus in a laccolith formed under a great thickness of sediments, the phenocrysts would be spoken of as the constituents formed in the intratelluric period, that is a lower, earlier period of the magma and in contrast to the groundmass, which is never spoken of in these cases as intratelluric.

Whatever exact ideas writers may have had regarding this term, it may be taken as well assumed that it means a deeper and therefore earlier stage of the magma in the earth's crust, than any in which the intrusive porphyritic rocks have been formed.

Two classes of phenocrysts.—Phenocrysts may be divided into two general classes. First, those which are found only as distinct porphyritic crystals and do not occur as a mineral component of the groundmass, like the micas and hornblendes of many acid rocks, and the olivines of many basic ones; and second, those minerals which are formed both as phenocrysts and also in the groundmass, like the quartz and feldspar of

<sup>\*</sup> Lehrbuch der Petrographie, vol. i, p. 737 et seq, 1893.

<sup>+</sup> Laccolitic Mountain Groups, U. S. Geol. Surv., 14th Ann. Rep., 1895, p. 231.

acid rocks and the pyroxenes of basic ones. The second class may be termed *recurrent* phenocrysts, meaning that the mineral composing them occurs both as a phenocryst and in the groundmass; Rosenbusch suggests the term in speaking of the recurrence of mineral formation. The other, or first class will be called here monogenetic phenocrysts. This distinction is of importance, as it is chiefly with the recurrent phenocrysts that we shall have to deal.

The proofs that all phenocrysts of intrusive igneous rocks are not intratelluric, but have in many cases been formed in place, and contemporaneously with other constituents may be divided into two classes, those which are megascopic, that is to say, geological or may be observed in the field, and those which are microscopic, or to be gathered by a study of thin sections. The geological proofs will be considered first.

Evidence of contact zones.—In the case of many laccoliths, dikes, sheets and other intrusive masses of igneous rocks of the more acid feldspathic kinds, it has been observed that while the main rock masses are highly porphyritic, often containing phenocrysts of great size, they pass into peripheral zones, which may attain considerable width, in which such phenocrysts are entirely wanting. The border zone is often observed to be dense, aphanitic and totally without phenocrysts either great or small—the constituents are all of one period of formation and allotriomorphic in structure.\*

But if the magna contained phenocrysts before coming to rest, they should occur in the border zone as well as elsewhere. It will not do to suggest two separate intrusions in these cases, for the geological "mise en place," and the whole character of the occurrences, utterly forbids such a supposition. Nor will it do to say that they previously existed in the border zone, but were redissolved. For the border zone being the part cooled first and most quickly, if they previously existed in it, then there is especially the place where they should occur. If any re-solution should take place, it would be in the center, not at the sides. Nor will it do to partially compromise the matter by saying that in the original magma they were very small and grew greatly after the magma came to rest.

No doubt this often does happen, but in many cases, as stated above, there are *none* in the contact zone, nothing to represent the thickly swarming masses of them in the central portion. In these cases the writer sees no escape from the conclusion, that the phenocrysts were formed in place. The evidence is most common and striking in regard to phenocrysts of the recurrent type, but it has been also observed in those of the monogenetic type.

\* Zirkel mentions similar instances, loc. cit., p. 740.

Evidence of dikes and sheets .- In many cases we have clear and indisputable evidence, that systems of dikes and sheets have been formed by a single geological act; that is, filled from a single parent magma, at the same time and under the same conditions, and they have of course the same chemical composition. An example occurring in the Judith Mts.\* of Montana has been recently described by the writer. The attendant fringing sheets lying above many laccoliths may also be cited as examples. Yet in many of these cases some sheets or dikes may have large and well-developed phenocrysts, others none at all. The laccolith may be full of phenocrysts; its attendant sheets or some of them may be entirely devoid of them. A sheet of tinguaite in the Judith Mts. contains phenocrysts of feldspar as large as one's hand, but a narrow sheet of the same rock which the general geologic history of the district shows was intruded at the same time, and which has a similar composition, has only very minute ones arranged in flow structure. In these cases, had they previously existed in the parent magma, they should be found in both alike. The conclusion in these cases is that the phenocrysts have formed in the places where they now are.

Evidence of fluidal phenomena.—In the case of some dikes and sheets it has been noticed that the phenocrysts of feldspar, which have a flat tabular form, have a definite arrangement throughout the mass, with the flat sides parallel to the bounding walls, or in other words, as it is commonly called, a "fluidal" or "flow structure." Sometimes they are rather irregularly distributed, collected in groups or in lines, and are just as apt to occur close to the border zone, at the bounding wall, as elsewhere in the dike. Such instances show clearly the effects of tabular plates being moved along in a liquid, and they prove that the phenocrysts were formed in the magma before it came to rest. How long before we are of course unable to determine, but in these cases they may be "intratelluric," so far as any definite meaning can be attached to this term.

In other dikes and sheets, the phenocrysts have no oriented arrangement in the mass, their orientation is wholly haphazard, they occur evenly distributed throughout, or they may be very small or of different character, or even wholly wanting in the border zones, and this in spite of the fact that they may have a pronounced tabular development.

If in the former cases mentioned the evidence proves that the phenocrysts were formed prior to injection, then the absence of such evidence, that is to say its converse, proves just as clearly that these flat phenocrysts were formed after injection when the magma had come to rest or in other words in place.

\* 18th Ann. Rep. U. S. Geol. Surv., pp. 551 and 572, 1898.

Moreover these flat phenocrysts, whether oriented or not, are of great value in throwing light on another question in theoretic petrology-whether phenocrysts ever move in the magma after it has come to rest; that is, whether they sink down in obedience to gravity. In the cases mentioned it is clear that they have not moved or they would have arranged themselves in obedience to the laws governing the movement downward of flat plates through fluids; they would be disposed with their flat sides downward or perpendicular to the walls of the dike. The writer has never seen such an occurrence nor been able to find any description of one, and until such a case has been found the evidence is against the idea that phenocrysts sink through gravity and evidently because the magma is too viscous. They could not assume such a position in an upward moving magina because the motion must be differential and would arrange them in the opposite direction; hence this orientation would show that they had moved and not the magma. The thicker accumulation of phenocrysts at the bottom of an intruded sheet, which has sometimes been noticed, would not prove they had fallen through gravity unless they had this arrangement, since that may merely show that the physical conditions necessary for the production of phenocrysts were more favorable and operative there than in the upper portion.

To return again to the formation of phenocrysts in place, from the evidences given above, when we find that in dikes and sheets flat tabular phenocrysts such as the feldspars of many acid rocks or the large mica tables of certain basic ones are scattered without orientation, we may conclude that they have been formed in place and are not "intratelluric."

Evidence of porphyritic granites.-It is well known that many granites contain large porphyritic feldspars, often of great size. The granites may have so coarse a grain that in the absence of these feldspars no one would think of them as other than typical granular rocks. The same is also true at times of other rocks besides granites. The evidence that these afford is chiefly of a negative kind, but it is useful to consider in this connection. It is evidence not so much of the time and place of the formation of phenocrysts as of the cause and *manner* of formation. To treat these questions fully would lead us into the discussion of the "*mise en place*" and the structure and classification of igneous rocks, which would be beyond the limits of this article. It will therefore be sufficient to ask one or two questions. Are these large phenocrysts of granites to be considered intratelluric or not, or is granite itself and all its constituents to be regarded as intratelluric? The difference between the porphyritic and the granular structures has been regarded by some, so far as their origin is con-

cerned, as a difference not alone of *degree* but of *kind*. If so, what is this precise difference and why should granular rocks ever possess a porphyritic structure?

What the significance of these crystals really is according to the author's belief will be shown later on.

Microscopical evidence.—We now come to those proofs which are to be seen in the minute internal structures of the phenocrysts when seen in thin section under the microscope. They may be divided into two classes, *external*, or to be seen in the minerals surrounding the phenocryst, and *internal*, to be seen in the minerals which the phenocryst encloses. We will consider the latter first.

Internal evidence .- While the majority of phenocrysts are homogeneous and free from inclusions, in a large number of cases they are not, but contain the other rock minerals. These are usually those of an older period of formation, such as apatites and ores, and their explanation appears simple, but in some instances the phenocrysts may enclose all the other rock minerals including crystals of the same mineral as they themselves are composed of. Thus large orthoclases are seen enclosing other orthoclases and quartz. If the enclosed mineral has the same composition and a similar orientation as the phenocryst, it becomes of course an integral portion of the crystal and the enclosure cannot be detected, but it often does not and is then readily identified. In these cases it is impossible to avoid the conclusion that not only was the phenocryst formed in place but contemporaneously with the other minerals. At such times the included minerals are scattered throughout the whole extent of the phenocrysts, but often they are found only in outer zones, indicating that the inner portion had formed first and that later the phenocryst was growing and expanding while the groundmass was crystallizing and was thus including it.\* The ability of crystallizing material to orient itself over considerable areas and enclose the other constituents is well illustrated in the poikilitic structure as seen in the quartzes of rhyolites, the orthoclases of shonkinites and the hornblendes and micas of the very basic rocks.

External evidence.—But growing and expanding phenocrysts do not always enclose the other minerals of the groundmass with which they come in contact. On the contrary, like all crystallizing substances, they endeavor to exclude impurities and more commonly they reject and push them along as they grow. Usually the minerals which make up the groundmasses of porphyritic rocks have an isodiametric development, they have therefore no orientation as regards form, and it is hence difficult to tell whether such particles lying alongside pheno-

\* These Montana instances give additional force to those mentioned by Zirkel in his discussion of the subject, loc. cit., p. 747.

crysts have been rejected and pushed or not. Iu certain cases the microlites of the groundmass have however an unequal development-they may be thin flat plates like the feldspars of some trachytes and andesites or slender rods like the ægirites of some phonolitic rocks. In such cases it is common to observe that the microlites have a length orientation parallel to each face of the large crystal forming the phenocryst, and not only this but the larger the phenocryst is, the more evident this becomes; they have been more crowded and the arrangement is more evident. This applies of course only to those microlites in the immediate neighborhood of the phenocryst. In the case of the large feldspar phenocrysts of some Montana tinguaites the crystals are covered with a perfect felt of similarly oriented ægirite needles.\* The arrangement is precisely what would happen if a scattered group of matches lying on a table should be swept to one side by a book and was caused without doubt by a quite similar process.

Such arrangements have been largely either overlooked or probably confounded with fluidal or flow structures. The latter, caused by movements or currents in the crystallizing magma, is however easily told, since in that case all of the constituents of the period are alike affected, both phenocrysts and microlites being drawn out into waving lines or streams, while in case the orientation is produced by the expansion of the phenocrysts the microlites are arranged parallel to each of its crystallographic faces, have no orientation in the interspaces and the phenocrysts themselves have also no orientation. This *expansion structure*—to coin a term for it—around phenocrysts may of course occur in combination with fluidal structure and merge into it, but typical cases of it are easily told and should be more generally noted in petrographic descriptions.

This evidence then goes to help the general proposition that some phenocrysts are formed in the places where they now are, for they were expanding and growing vigorously while the groundmass was crystallizing and a magma whose groundmass is crystallizing has already reached the place it is destined to occupy.

Summation of evidence.—The value of evidence is cumulative and increases, not in an arithmetical, but in a geometrical ratio. A single fact may indicate definitely a certain hypothesis as its explanation, but it may also be an exception to a general rule. When we can bring a second fact to support it, the probability of the correctness of the hypothesis is greatly increased, and when a considerable number of such facts are found, all pointing to the same explanation, we may reasonably consider it as proved. Thus, when we find that a dike contains flat tabular phenocrysts, which show no orientation, and are wanting in the border zone of contact and contain all the other

\* This Journal, IV, ii, 1896, p. 191.

rock constituents, and when this dike is one of a set filled by the same injection which may or may not have similar phenocrysts, we are thoroughly justified in assuming that its phenocrysts are formed in place and are not intratelluric.

Evidences of intratelluric origin.—We should now consider the evidences on which is based the view that phenocrysts have been formed at great depths under wholly different conditions from the other rock constituents. So far as the writer can discover, they are these,—the contrast in size and crystal form of phenocryst to the constituents of the groundmass, the fluidal arrangement the phenocrysts sometimes possess and the fact that they are often corroded or changed in character, that is resolved.

But the contrast of form and size, as we shall presently show, may be explained in quite a different way; the fluidal arrangement certainly shows that the phenocrysts were formed before the magma came to rest, but it does not show how long before or that it may not have been just previously; while the corroded and altered crystals show a change of *conditions*, not necessarily a change of *place*, and although this may be a logical inference it is still not the only one.

From the facts at our command, therefore, it appears most reasonable to say that in some cases we know that phenocrysts have been formed in place; in other cases we know that they were formed prior to injection, but how long and how far we do not know, and that in the great majority of cases we do not know whether they were formed in place or not. It is the author's belief that the majority are formed in place for reasons which it is now proper to give.

Conditions governing the formation of rock structure.—So far as the writer can understand, the French believe in two distinct and different periods of consolidation for all intrusive rocks both granular and porphyritic; many if not most of the Germans believe in one for the granular and two for the porphyritic; like some petrographers, the writer sees no necessity for more than one in both.

The conditions governing the consolidation and crystallization of an igneous magma are complex, and many of them, perhaps all, are as yet ill understood. The fall of temperature is the most important, but the chemical composition of the magma, the influence of mineralizing vapors and the pressure are also of great importance. Another important consideration which has been greatly overlooked is increasing viscosity, which depends on chemical composition and temperature. It would be impossible to discuss all these in full, and the writer therefore confines himself to a brief statement of his own views.

The greatest determinant in the formation of rock structure is the ratio of time in the fall of temperature between the point where the insolubility and crystallizing moment of a compound begins to the increasing viscosity. Suppose a fluid rock magma, without crystallizations in it, comes to rest and the temperature begins to fall. At a certain point compounds, the ferro-magnesian ones let us say, commence to separate. The fall has been so gradual that only a few centers of crystallization have been set up. The magma retains its fluidity for each period and each mineral has a considerable time in which to grow, orienting and assimilating its substance around it or, to coin a phrase, it has a long crystallization interval. It is theoretically possible that if the conditions are stable for a long enough period each mineral in turn may exhaust itself in the magma before the next begins. Usually there are overlaps. Thus the process goes on until each has had its turn, the rock has crystallized and the granular structure is formed.

Other things being equal, the granularity depends on the length of the crystallization interval. In the case of the very siliceous magmas we must take into account another factor, the viscosity, which depends greatly on the included water vapor. If this is present in large amount the fluidity of the magma is enormously increased, and with it the radius of action of each crystallizing center, that is, the crystal has a free chance to grow, orient material and expand. On the other hand, if there is little or no water vapor present or it escapes before crystallization begins, the viscosity is greatly increased, the radius of action of each center is small, and, although the crystallization interval may be sufficiently long, the crystals are restrained in their growth, new centers are set up and the rock is finegrained. Hence we may have coarse granular and fine granular rocks without porphyritie structure.<sup>\*</sup>

In the case of the basic rocks, the included water vapor has no such function, their viscosity increases at a vastly slower rate for each degree in fall of temperature, hence the radius of action for equal crystallization intervals is much larger than in the acid rocks and we therefore find them quite coarse granular under the same conditions which have produced fine-grained structures in the acid ones. Other things being equal, the granularity depends on chemical composition, but there is also a limit to this, for it also depends on the number of crystallization centers which have been set up.

*Porphyritic structure.*—We can now consider the porphyritic structure. Suppose that an acid magma is injected with included water vapor and that the fall of temperature is comparatively rapid. The vapors escape rapidly and with the cooling and their escape the viscosity augments in a greatly

\*See also Iddings' Crystallization of Igneous Rocks, Bulletin Phil. Soc., Washington, vol. xi, p. 105, 1889.

increasing ratio. This means shorter and shorter crystallization intervals for the various components as their periods commence. Thus the earlier ferro-magnesian components may have time to grow to considerable size while the increasing viscosity forces the feldspars and later components to be of very small size. Thus we may have a porphyritic structure with phenocrysts of the monogenetic type as a result of a single process of crystallization. It may be considered a sort of arrested or retarded granular structure.

But phenocrysts of the recurrent type evidently demand a further explanation and this is to be sought in two things. First the writer believes that the influence of mass action is of great importance and that compounds which are present in relatively large or predominant amount tend to set up centers of crystallization before what might otherwise be the proper period for that component. The rest of the process might go on as noted above and a porphyritic structure would be formed with phenocrysts of the recurrent type. Phenocrysts of the recurrent type would then consist of those minerals which are present in largest amount, and this is generally true. Such phenocrysts might form at any time and the earliest would be crystallizing during the whole period and might include the other constituents or exclude and orient them as previously noted.

Second, the writer is inclined to believe that too great regularity in the period of commencing crystallization of the different components has been ascribed to crystallizing magmas. That the different minerals *tend* to have their proper periods is undoubtedly so, but they do not always have them, and, for example, centers of feldspar crystallization may be set up at different times resulting in porphyritic structure as mentioned above. If we dissolve salt in water and allow the solution to crystallize in different beakers, we may obtain under apparently similar conditions a few large crystals, many small ones or a mixture of large and small. The conditions are of course not exactly similar but the differences may be very slight.

The more coarsely granular the rocks are, the more stable, and even the conditions under which they have crystallized and the less likelihood there is for the formation of phenocrysts—yet these do occasionally occur, as noted above in the porphyritic granites. In the fine-grained rocks these conditions are changed, the causes mentioned above become operative and a porphyritic structure is liable to result, as it commonly does.

Thus it seems most reasonable to regard the majority of phenocrysts as formed in place though in some cases they have evidently formed previously while the magma was ascending. Even in these cases they have probably been formed not long before.

Yale University, New Haven, Conn, December, 1898.

## ART. XXIX.—On the Occurrence, Origin and Chemical Composition of Chromite; by J. H. PRATT.

Introduction.—In a recent paper\* on the origin of the corundum associated with the peridotites in North Carolina, attention was called to the constant presence of the mineral chromite in these rocks. During the past summer the occurrence of chromite has been carefully studied and the occurrences in North Carolina have been examined in the field. As a result of these examinations the author has been led to adopt the theory that the chromite should be regarded as having been formed at the same time with the peridotite, i. e., as having been held in solution by the molten mass of the peridotite and crystallized out among the first minerals as the mass began to cool.

This theory is essentially the same as that advanced by the author<sup>+</sup> for the origin of the corundum associated with the peridotite rocks, and a similar line of reasoning has been used to substantiate the theory proposed.

Investigations concerning the igneous origin of some of the ores have been materially aided, during the recent years, by the able experiments of Morozewicz<sup>+</sup> and Lagorio<sup>§</sup> and by researches that show us more clearly why we should regard a fused mass of rock as a liquid, having similar properties to an ordinary solution. The fused mass of rock is capable of holding different minerals in solution and as the molten mass begins to cool, these minerals would separate out not according to their fusibility but according to their solubility in the fused The more basic minerals being the more insoluble mass. would be the first to separate out, and as was mentioned in the paper already referred to, this crystallizing or solidifying out from the molten mass would take place first on its outer boundaries, for here it would cool first. Convection currents would tend to bring new supplies of material to the outer zone where crystallization takes place.

Occurrence.—With the exception of alluvial deposits, chromite has only been found in the peridotite and allied igneous basic magnesian rocks, or in the serpentines which have resulted from the alternation of these rocks. In the North Carolina peridotites chromite occurs more commonly as scattered grains or crystals, but it is also to be found in the form of imbedded masses near the boundaries of the lenticular bodies of dunite.

> \* This Journal, vol. vi, p. 49, July, 1898. † This Journal, vol. vi, p. 50, July, 1898. ‡ Zeitschr für Kryst, vol. xxiv, p. 281, 1895. § Ibid., p. 285.

AM. JOUR. SCI.—FOURTH SERIES, VOL. VII, NO. 40.—APRIL, 1899. 19 It does not occur in well defined veins, but is often in masses or pockets which apparently have no relation whatever to each other. But few writers on the occurrence of chromite have described the relation of the chromite deposits to the rock in which it is found. One or two have mentioned the chromite as being found near the eastern boundary of the serpentine or at the northern border of the serpentine belt, but no definite description of the occurrence could be obtained. The large deposits of chromite in North Carolina occur in the peridotite rock and near the contact of this rock with the enclosing gneiss. Also where there is but a small amount of chromite either in small pockets or in grains or crystals, these are more abundant near the contact and diminish in number toward the center of the mass of the peridotite.

Where these large deposits of chromite occur there has been no corundum or but very little found, and where we find the large deposits of the corundum there is a scarcity of chromite.

This constant occurrence of the chromite in rounded masses of varying proportions near the contact of the peridotite with the gneiss, its occurrence in the fresh as well as in the altered peridotite, indicate that the chromite has been held in solution in the molten mass of the peridotite when it was intruded into the country rock and that it separated out among the first minerals as the mass began to cool.

As has been said, the peridotite (dunite) magma holding in solution the chemical elements of the different minerals would be like a saturated liquid, and as it began to cool the minerals would separate or crystallize out, not according to their fusibility but according to the degree of their solubility in the molten magma. The more basic minerals, according to the general law of cooling and crystallizing magmas, being the less soluble. would therefore be the first to separate out. These would be the oxides containing no silica and in the present case would be the chromite, spinel and corundum. These minerals would solidify or crystallize out where the molten magma first began to cool, which would be at the contact of the mass with the country rock; convection currents would tend to bring new supplies of material to the outer boundary which would deposit its chromic oxide as chromites. This would account for all the irregularities of the chromite deposits : their pocket-like nature, the shooting off of apophyses from the main masses of the chromite into the peridotite, the widening and pinching of the chromite lodes, and the apparently non-relation or connection of one pocket of chromite with another. There has not been enough work done in the North Carolina chromite mines to demonstrate the exact position and relation of the chromite deposits to the gneiss or the country rock, and in the description of other chromite mines but little light has been thrown on this point.

The chromite would be concentrated near the borders of the peridotite in rounded masses, with offshoots penetrating into the peridotite. The line of contact near the gneiss would be sharp and nearly regular, while with the peridodite the contact would be very irregular.

In prospecting for either chromite or corundum the largest and richest deposits may be expected near the contact of the peridotite with the gneiss or other country rock.

Chemical composition.—Chromite has been analyzed from the following localities in North Carolina: Price's Creek, six miles southwest of Burnesville, Yancey County; Webster, Jackson County; and Corundum Hill, Macon County.

Pure material for analysis, showing no impurities when examined with the microscope, was readily obtained by hand picking.

The mineral was fused several times with bisulphate of potash, then taken up with hydrochloric acid and silica tested for. Iron, aluminium and chromium were precipitated with ammonia, the precipitation being made at least three times. Magnesium, calcium and manganese were determined in the filtrates by the usual methods.

The precipitate of the mixed oxides was dissolved in hydrochloric or nitric acid and the excess of acid evaporated. Sodium hydroxide was then added in excess and chlorine passed into the hot solution. The solution was acidified and the iron and aluminium precipitated twice with ammonia and weighed as mixed oxides. These mixed oxides containing a trace of chromium were fused with acid potassium sulphate, digested with water and acidified. One precipitation was made with ammonia to partially remove sulphates. This precipitate was dissolved in hydrochloric acid and treated as before, the iron and aluminium being obtained free from chromium. The iron was determined volumetrically.

To the filtrates containing the chromium, alcohol and hydrochloric acid were added and the solution digested for some time. The chromium was precipitated as hydroxide and weighed as  $Cr_2O_a$ . To ensure the purity of the precipitate, it was fused with four parts of sodium carbonate to one part of potassium nitrate, the fusion taken up with water and tested for magnesium.

A number of experiments were made to determine the ratio of ferric to ferrous oxide, but they were all unsatisfactory. By digesting the very finely powdered mineral in a mixture of hot concentrated hydrofluoric and sulphuric acid, in an atmosphere of carbon dioxide for half an hour, enough of the mineral was decomposed to show the presence of ferric oxide.

The analyses were made by Dr. Chas. Baskerville\* and Dr. H. W. Foote.

The result of the analyses were as follows:

Price Creek.‡	Ratio.	Corundum Hill.‡	Ratio.	Webster §	Ratio.
Cr.O 59.20	·386	57.80	·377	39.95	.261
Al <sub>2</sub> O <sub>3</sub> 7.15	.070	7.82	.076	29.28	.287
FeO 25.02	$\cdot 347$	25.68	.356	13.90	.193
MgO 4·42	·111	5.22	·131	17.31	•433
SiO <sub>2</sub> 3.20		2.80			
MnÖ '92		•69			

In the above analyses the ratio of the bivalent oxides to the trivalent oxides is uniformly high and can probably be accounted for by reason that some of the iron calculated as ferrous oxide was in the ferric state, as was proved in the Webster chromite.

Taking enough of the Cr.O. and MgO to unite with the FeO and Al, O, respectively to form the molecules FeO. Cr.O., and MgO. Al<sub>o</sub>O<sub>3</sub>, there remains approximately enough of the Cr<sub>2</sub>O<sub>3</sub> to unite with the excess of the MgO to form the molecule MgO. Cr.O. The nearer the ratio of the bivalent oxides equals that of the trivalent oxides, the nearer the excess of the Cr<sub>2</sub>O<sub>3</sub> and MgO equal each other. The inability to determine the ratio of the ferrous to the ferric oxide in the above analyses prevents the obtaining of a sharp ratio in the excess of the Cr.O. and MgO.

With the exception of two cases, in all the terrestrial chromite analyses examined, alumina and magnesium were invariably present, varying from a small per cent in some samples to others that showed the presence of more than 20 per cent of these oxides. In the above analyses and in most of the others examined, it was noticed that the magnesia usually varied with the alumina, those rich in alumina being correspondingly rich in magnesia.

This constant occurrence of magnesia and alumina in the chromite would seem to indicate that the molecule of the mineral now called chromite is not pure FeO. Cr.O. but is a combination of the three isomorphous molecules, FeO. Cr.O.; MgO. Cr.O. and MgO. Al.O.

But two analyses of chromite (terrestrial) have been found that do not show the presence of magnesia and alumina, the first a magnetic chrome sand from Chester, Pa., analyzed by T. H. Garrett, in which all the iron is calculated as ferric

Baskerville.

This Journal, vol. xiv, p. 47, 1852.

<sup>\*</sup> Of the Chemical Laboratory, N. C. Geological Survey.

<sup>+</sup> Of the Sheffield Laboratory, Yale University. § Foote.

oxide, and the second chromite from Vache Island, West Indies, analyzed by J. Clouet.\*

	I (Garrett).	II (Clouet).
Cr.,O	41·55 ´	51.53
FeO		48.46
Fe.O	62.02	
SiO <sub>2</sub>	1.25	
•		
	104.82	99.99

A greater part of the iron in Garrett's analyses is undoubtedly in the form of ferrous oxide, as is indicated by the high per cent obtained. From the above, it is seen that a pure chromite having the composition  $FeO \cdot Cr_2O_3$  is not common in nature.

The MgO. Al<sub>3</sub>O<sub>3</sub> occurs nearly pure in nature as normal spinel. The normal MgO.  $Cr_2O_3$  has not been found in nature, but, as indicated from the above analyses, there is good reason to believe that this molecule does exist, and we may expect to find normal MgO.  $Cr_2O_3$  occurring as a definite mineral. Under this theory of the composition of the chromite, the formulæ for the three chromites described in this 'paper would be as follows:

1.	Price Creek	$10 \text{FeO} \cdot \text{Cr}_{\circ} \text{O}_{\circ};$	MgO. Cr.O.;	2MgO.Al.O.
2.	Corundum Hill	9FeO . Cr.O.;	MgO. Cr.O.;	2MgO.Al <sub>2</sub> O <sub>3</sub> .
3.	Webster	$FeO.Cr_2O_3;$	$MgO.Cr_2O_3;$	2MgO.Al <sub>2</sub> O <sub>3</sub> .

The first two formulæ will represent approximately those of the majority of the chromites that have been found, and they are approaching the normal chromite FeO.  $Cr_2O_3$  as their limit.

As the FeO. Cr<sub>2</sub>O<sub>3</sub> molecule decreases and the MgO. Al<sub>2</sub>O<sub>3</sub> increases the mineral would approach normal spinel MgO. Al<sub>2</sub>O<sub>3</sub> as its limit, the mineral picotite or chrome spinel being representative of a mineral near the spinel end.

M. E. Wadsworth, † in comparing the chromite with the picotite associated with peridotites, says :

"It is probable that picotite and chromite belong to the same mineral series, the term picotite being more commonly applied to the freshest states, and that of chromite to those forms more altered, and to the local aggregations arising from the migration of the chromic oxide during the alteration of the associated peridotite rocks. As a further extreme in the alteration a change to a more or less magnetite occurs." These conclusions are deduced from a microscopical study of these minerals."

\* Ann. Chim. Phys., vol. xvi, pp. 90-100, 1869; and Wadsworth's Lithological Studies, appendix. p. iv.

+ Lithological Studies. p. 184.

The author does not agree with Dr. Wadsworth that the chromite represents an altered product of a mineral, of which picotite is a purer form. The chromite is a mineral which suffers alteration but slightly and, as it is found at the present time, represents the original mineral and not an altered form. The difference in the microscopical properties can readily be accounted for by the difference in the chemical composition. With an increase in the ratio of the molecule, MgO. Al<sub>2</sub>O<sub>3</sub> and a corresponding decrease in the molecule, FeO.  $Cr_2O_3$ , the more translucent the mineral will become.

These two minerals belong to the same group and are closely allied to each other, and they represent two primary minerals and not different stages in the alteration of another mineral.

In the analysis of the Webster chromite, the largest percentage of MgO was obtained and in the calculation of the ratios the formula was shown to be FeO.  $Cr_2O_3$ ; MgO.  $Cr_2O_3$ ; 2MgO.  $Al_2O_3$ , this being the highest ratio of the molecule MgO.  $Cr_2O_4$  of any chromite examined. The theoretical composition is here given, together with the analysis of the Webster mineral:

Webster chromite found.	Theory for $2 MgO.Al_2O_3$ ; $MgO.Cr_2O_3$ ; FeO.Cr_2O_3.
Cr.O 39 95	40.90
Al O 29 28	30.44
FeO 13.90	10 75
MgO 17·31	17.91
100.44	100.00

This analysis is similar to that described by Bock\* for a "magnochromite" from Grochau, Silesia, which contained Cr<sub>2</sub>O<sub>4</sub> 40.78, Al<sub>2</sub>O<sub>2</sub> 29.92, FeO 15.30 and MgO 14.00.

In appearance this Webster chromite is different from any that has come under the author's observation, being much more of a coarse-grained appearance than ordinary chromite.

In order to designate this Webster chromite and others of similar composition, the author proposes the name, *Mitchellite*, in honor of the late Professor Elisha Mitchell of North Carolina.

N. C. Geological Survey, December, 1898.

\* Zs. G. Ges., xxv, p. 394, 1873.

J. T. Norton, Jr.—Titrations by Sodium Thiosulphate. 287

ART. XXX.—The Influence of Hydrochloric Acid in Titrations by Sodium Thiosulphate, with special reference to the Estimation of Selenious Acid; by JOHN T. NORTON, JR.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXX.]

In the method of Norris and Fay\* for the iodometric determination of selenious acid, advantage is taken of a direct and unique action of sodium thiosulphate upon selenium dioxide in the presence of hydrochloric acid. Most excellent results are claimed for this method; but the explicit statement of the originators of the method, that the amount of hydrochloric acid present does not influence the result, provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate, as to suggest the necessity of careful investigation of this point.

Pickering, † in his investigation of the reaction between iodine and sodium thiosulphate, has shown that more iodine is required to oxidize the thiosulphate as the proportion of hydrochloric acid increases. He ascribed this effect to the formation of a sulphate, apparently, by the increased activity of the iodine, but the more rational explanation is that, although some sulphate is ultimately formed, the thiosulphate is first partially decomposed into free sulphur and sulphur dioxide. Finkenert and Mohr§ also mention the decomposing effect of free acid upon sodium thiosulphate.

The sodium thiosulphate used in the following experiments was taken in nearly decinormal solution and was standardized by running it into an approximately decinormal solution of iodine, the value of which had been determined by comparison with decinormal arsenious acid made from carefully resublimed arsenious oxide. In the experiments of Table I the solutions were stirred continuously and kept at a temperature of from 0° to 5° C., while the thiosulphate ran into the acidified The volume of the solution, though fixed at the beliquid. ginning as given in the table, was considerably increased during the operation by the melting of the ice. Titrations were conducted as rapidly as possible to avoid the separation of sulphur, which is likely to occur, especially when the acid and thiosulphate are present in large quantities. A perusal of the table

\* Am. Chem. Jour., vol. xviii, pp. 703. † Jour. Chem. Soc, vol. xxxvii, pp. 135. ‡ Anal. Chem., 6 Aufl., pp. 620. § Titrirmethode, 6 Aufl., pp. 279.

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shows that the influence of the hydrochloric acid upon the thiosulphate depends chiefly upon the amount of the thiosulphate present and afterwards upon the degree of dilu-

TABLE I.

Volume of liquid at	$\mathrm{Na_2S_2O_3}$ approximate	ly Volu	Volume of $\frac{N}{10}$ iodine used in titration.			
titration.	$\frac{n}{10}$ taken.	HCl=none.	$=1 \text{ cm}^3$ .	$=5 \text{ cm}^3$ .	$=10 \text{ cm}^3$ .	
$\mathrm{cm}^{8}$ .	$\mathrm{cm}^{3}$ .	cm <sup>3</sup> .	cm <sup>3</sup> .	$\mathrm{cm}^{3}$ .	$\mathrm{cm}^3$ .	
100	30	30.25	30.75	30.76	31.2	
200	66	30.22   mea	n= 30.21	30.26	31.4	
300	66	30.20 30.2	2 30.22	31.03	30.9	
400	٤٤	30.21	30.20	30.20	30.55	
500	"	30·20 j	30.20	30.21	30.55	
100	25	25.29	25.32	25.98	25.70	
200	"	25.28   mea	n = 25.34	25.40	25.45	
300	ډډ	25.29 > 25.2	7 25.41	25.38	25.83	
400	66	25.27	25.24	25.30	25.63	
500	• 6	25·22 J	25.23	25.40	25.30	
100	20	20.15	20.17	20.33	20.23	
200	٠٠	20.20   mea	n = 20.13	20.27	20.23	
300	"	20.21 \$ 20.1	5 20.15	20.20	20.17	
400	"	20.20	20.10	20.27	20.07	
500	"	20.10	20.10	20.17	20.13	

tion and its own absolute quantity. Thus when  $30^{\text{cm}^3}$  of sodium thiosulphate were employed the effect of  $10^{\text{cm}^3}$  of acid is marked at all dilutions within the range of the experiments; the effect of  $5^{\text{cm}^3}$  of acid is inappreciable only at a dilution of from 400 to  $500^{\text{cm}^3}$ , and when  $1^{\text{cm}^3}$  of acid is employed the effect is only perceptible at a volume of  $100^{\text{cm}^3}$ . When  $25^{\text{cm}^3}$ of the thiosulphate were used the influence of the acid is less marked; for at a dilution of  $500^{\text{cm}^3}$  the effect of  $10^{\text{cm}^3}$  of acid is not seen, and  $20^{\text{cm}^3}$  of the thiosulphate may be present at any dilution down to  $100^{\text{cm}^3}$  in the presence of as much as  $10^{\text{cm}^3}$ of the acid, and even considerably more, as experiments not included in the table indicated.

The slight discrepancies which appear occasionally in the table were due, no doubt, to unavoidable differences in the time of action.

This influence of time upon the reaction between sodium thiosulphate iodine and hydrochloric acid comes out clearly in the following series of experiments, in which the thiosulphate was run into the acidified water, cooled to a temperature of from 0 to 5° C. by means of ice, the solution being allowed to stand 5, 10, and 15 minutes. Sulphur was thrown down in nearly every case.

		**
11.4	DIT	
14	DLL	±1.

Volume of the liquid at beginning of	HCl sp gr.(112)	$Na_2S_2O_3$ approximately $\frac{N}{2}$ taken	Volume of $\frac{N}{10}$ iodine used in titration after standing.		
titration.	present.	10 taxen.	5 min.	10 min.	15 min.
cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	$cm^3$ .	cm <sup>3</sup> .	cm <sup>3</sup> .
200	10	30	30.80	31:30	32.32
66	"	25	25.50	26.00	26.30
"	" "	20	20.30	20.70	20.68

The results of the table emphasize sufficiently the necessity of proceeding as rapidly as possible with the titration of sodium thiosulphate by iodine in presence of hydrochloric acid, when the thiosulphate is present in considerable amount. As would be expected, the effect of temperature upon the reaction is also marked. In the following experiments the sodium thiosulphate was run into the acidified water, previously heated to the temperature indicated, and then titrated with iodine.

TABLE III.

Volume of liquid at beginning of titration.	HCl. sp. gr. (112) taken.	Temp. Centigrade.	$\frac{\text{Na}_{2}\text{S}_{2}\text{O}_{3}}{\text{approximately.}}$ $\frac{N}{10} \text{ taken.}$	Volume of $\frac{N}{10}$ iodine used in ti- trations at differ- ent temperatures.
cm <sup>3</sup> .	cm <sup>3</sup> .	С.	$\mathrm{cm}^{3}$ .	cm <sup>3</sup> .
400	10	$6^{\circ}$	25	23.52
"	"	$22^{\circ}$	66	23.73
"	٤٢	$34^{\circ}$	66	24.35
۵۵	66	$42^{\circ}$	66	24.5
"	ç ¢	54°	"	25
"	66	64°	" "	26.1

From these results it is plain that the conditions under which considerable amounts of sodium thiosulphate are titrated in presence of hydrochloric acid must be carefully guarded when accuracy is a consideration. It is also apparent that in all cases the temperature should be reduced as nearly to 0° C. as possible and rapidity of titration by the iodine is an essential. So long as the thiosulphate present does not exceed  $20^{\rm cm^3}$  of the  $\frac{n}{10}$  solution, rapid titration in cold solution proceeds with fair regularity in presence of hydrochloric acid up to  $10^{\rm cm^3}$  of the acid of sp. gr. 112. When, however, the amount of thio-

sulphate is greater than  $20^{\text{cm}^3}$  of the  $\frac{n}{10}$  solution, care as to the

restriction of the acid and dilution of the solution becomes a necessity. Fortunately, in most analytical processes involving the use of the thiosulphate it is possible to add that reagent from the burette to the solution to be acted upon, so that it is destroyed normally as fast as it is introduced and the danger of interaction with the acid does not occur. In the process of Norris and Fay, however, the method involves the addition of an excess of the thiosulphate to the solution of selenious and hydrochloric acids, and thus the conditions prevail which demand care as to the relation of the acid, the thiosulphate and the degree of dilution. I have experimented, therefore, with this process under varying conditions.

The process of Norris and Fay for the iodometric determination of selenious acid consists briefly in treating the solution of that acid in ice water, in the presence of hydrochloric acid, with an excess of a  $\frac{n}{10}$  solution of sodium thiosulphate and titrating back the excess of the thiosulphate with iodine. Four molecules of sodium thiosulphate act, apparently, upon one molecule of selenious acid according to a reaction which the authors propose to study.

The selenium dioxide used was made by dissolving presumably pure selenium in nitric acid and evaporating to dryness. The residue was then treated with water, and a little barium hydroxide was added to remove any sulphate which might be The solution was then filtered and the filtrate present. evaporated to dryness. The residue was mixed with four or five times its volume of dried pulverized pyrolusite, and the whole was put into a porcelain crucible and heated. The sublimate of selenium dioxide was carefully collected on a dry watch-glass and put into a drying bottle as quickly as possible. The pyro-lusite prevents any reduction of the selenium dioxide to selenium and the product consisted of beautiful long white needles. This method of preparing the selenium dioxide, which has been used for some time in this laboratory, avoids contamination of the selenium dioxide by nitric acid or water, resulting from the decomposition of the latter, which would be possible in case this reagent were employed in the final sublimation, as is recommended by Norris and Fay. The hydrochloric acid used was of a sp. gr. 112, as recommended by the originators of the process. For the experiments of Table IV the dilution at the beginning was fixed at 400cm<sup>3</sup>, and this was increased in every case by the melting of the ice used to cool the liquid. A glance at the preceding part of this paper

will show that at this degree of dilution the hydrochloric acid present has the least effect.

TA	RI	E.	17	<b>7</b>
T U	101		-	•••

		$\underset{\text{SeO}_2}{\text{Amount}}$	HCl sp. gr.	at begin- ning of	Excess Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$SeO_2$	
		taken. grm.	112 taken. cm <sup>3</sup> .	titration. cm <sup>3</sup> .	employed. cm <sup>3</sup> .	found. grm.	Error. grm.
(	(1)	·0616	10	400	<b>2</b> ·28	0.0625	0.0003 +
l	(2)	.0628	66	"	7.11	0.0631	0.0003 +
(	(̀3)́	.0508	دد	44	11.4	0.0211	0.0003 +
(	(4)	.0587	66	"	12.8	0.0594	0.0007 + mean
(	(5)	.0807	66	66	15.3	0.0813	0.0006 + .00005 +
ĺ	(6)	·0633	66	"	20.85	0.0638	0.0005 +
(	(7)	.0682	25	66	1.11	0.0685	0.0003 +
(	(8)	.0779	66	66	1.35	0.0288	0.0006 +
(	(9)	·0465	66	66	18.93	0.0469	0.0004 +

These results, while not so good as those obtained by Norris and Fay, are satisfactory and show that at this degree of dilution the process is accurate. These results accord closely with those contained in Table I. At a dilution of  $400^{\rm cm^3}$  or in the presence of only  $20^{\rm cm^3}$  of sodium thiosulphate in excess the hydrochloric acid present had no perceptible effect. Of course, it must be kept in mind that the hydrochloric acid acts only upon the excess of thiosulphate which is not taken up by the selenium dioxide. The slight constant plus error in these results cannot be accounted for by errors in the standards; they were all carefully determined. Another preparation of selenium dioxide was made, starting with pure selenium carefully precipitated by sulphurous acid, before putting it through the course of treatment previously described, and the results obtained by the action of the sodium thiosulphate recorded in Table V agree closely with those of the preceding table.

#### TABLE V.

A	mount	HCl	$H_2O$	$Na_2S_2O_3$		
	SeO <sub>2</sub>	sp. gr.	at	in	SeO 2	
t	laken.	112.	beginning.	excess.	found.	Error.
	grm.	¢m³.	$cm^3$ .	$\mathrm{cm}^{3}$ .	grm.	grm.
(1)	·0562	10	400	9.52	•0566	.0004 +
(2)	.0651	25	66	11.20	0655	.0004 +

The next step was to determine the effect of diminishing the dilution and of varying the strength of acid. The following table gives the results of my experiments.

	Amount of SeO <sub>2</sub> taken. grm,	$egin{array}{c} Volume \ of \ H_2O \ at \ begin-ning. \ cm^3 \end{array}$	HCl sp. gr. (112). cm <sup>3</sup>	$egin{array}{c} { m Excess} \\ { m of} \ { m Na}_2 \\ { m S}_2 { m O}_3. \\ { m cm}^3 \end{array}$	SeO2 taken. grm.	Error. grm.
(1)	$\cdot 1042$	200	5	24.16	.1041	·0001 —
(2)	·0611	"	10	13.3	·0611	$\cdot 0000 \pm$
(3)	.0850	"	10	21.9	.0828	.0022 -
(4)	.0757	"	25	13.07	·0749	.0008-
(5)	.0540	"	25	21.02	$\cdot 0522$	.0018-
(6)	·0674	300	5	10.04	.0679	·0005+
(7)	.2416	400 .	5	15.9	·2424	·0008+

#### TABLE VI.

It is apparent that at the dilution of  $200^{\rm cm^s}$  we run into difficulties, and the greater the excess of thiosulphate present the greater is the error. When the amount of sodium thiosulphate exceeds  $20^{\rm cm^s}$  a reduction in the amount of acid to  $5^{\rm cm^s}$  is plainly of advantage, as is shown in a comparison of Exps. (1), (3), and (5), and is not disadvantageous at larger dilutions and with smaller amounts of the thiosulphate, as shown in Exps. (6) and (7). The necessity of placing some limits on the method of Norris and Fay has now, I think, been established. The excess of the thiosulphate must be carefully regulated, as well as the temperature. If one has knowledge of the approximate amount of selenious acid in solution, this is not a matter of great difficulty, and things should be so arranged that no more than  $20^{\rm cm^s}$  of the  $\frac{n}{10}$  thiosulphate should ever

be present in excess of the amount necessary to reduce the selenious acid. If this limit —amounting to  $0.0400^{\rm cm}$  of SeO<sub>2</sub> is placed upon the thiosulphate, so much as  $10^{\rm cms}$  of hydrochloric acid (sp. gr. 112) may be present without endangering the accuracy of the process, provided the solution is diluted to  $400^{\rm cms}$  at the outset; if only  $5^{\rm cms}$  of hydrochloric acid are present, the volume at the beginning may be reduced with safety to  $200^{\rm cms}$ . At all events,  $5^{\rm cms}$  of the hydrochloric acid are amply sufficient to bring about the reaction between the thiosulphate and the selenium at any dilution within the range of my experiments. With these precautions taken, the process of Norris and Fay is simple, rapid and accurate; without them, as the experimental results indicate, errors of considerable amount may enter.

According to the method of \* Muthmann and Shafer, the determination of selenious acid is effected by the simple addition of potassium iodide to the acidulated solution of selenious

\* Berichte d. d. Chem. Gesell., xxvi, 1008.
acid, and the iodine set free is titrated with sodium thiosulphate. In this procedure the thiosulphate is taken up by the iodine as it is added to the solution, so that the danger of any action between the thiosulphate and the acid is out of the question. It was shown in a former paper from this laboratory \* that this simple method is inaccurate on account of the iodine evolved. In a later article also from this laboratory † it was shown that selenium may be completely precipitated and determined with accuracy gravimetrically provided the amount of potassium iodide employed is enormously in excess of that theoretically required. This suggests naturally the trial of very large excesses of potassium iodide in the process of Muthmann and Shafer. The details of experiments made in this manner are given in the following table.

## TABLE VII.

				HCI		
	$SeO_2$		Vol. of	sp. gr.	SeO <sub>2</sub>	
	used.	KI.	solution.	(112).	found.	Error.
	grm.	grm.	$cm^3$	$\mathrm{cm}^3$	grm.	grm.
(1)	.0553	10	150	10	.0558	.0005 +
(2)	.0574	5	66	"	0567	.0007 —
(3)	*0683	5	66	"	.0683	$\pm 0000 \pm$
(4)	.0487	5	66	"	·0484	.0003 -
(5)	2617	10	66	66	2589	·0028-
· ·						

It is obvious that for small quantities of selenium dioxide the accuracy of the process is very much increased by the use of large amounts of iodide, though, of course, the difficulty in reading the end reaction due to the presence of precipitated red selenium still remains; but the process is still inaccurate when large amounts of selenium dioxide are employed.

In conclusion I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

\* This Journal, Gooch and Reynolds, vol. 1, 254. + Peirce, this Journal, vol. i, 1896, p. 416.

# ART. XXXI.—Some Rock-forming Biotites and Amphiboles ;\* by H. W. TURNER, with analyses by W. F. HILLEBRAND, H. N. STOKES, and WILLIAM VALENTINE.

THE minerals referred to in this paper were separated from the rocks containing them by means of the Thoulet solution. The analyses were made in the laboratory of the U. S. Geological Survey, the object being to furnish a basis for calculating the molecular composition of the rocks containing them. All of the material was fresh and sensibly free from foreign particles. The powder analyzed in each case was examined microscopically and such impurities as were found are given. Samples of minerals as well as chips of the rocks containing them will be sent to any one who is investigating rock-forming minerals, upon request. The specimens came from the Sierra Nevada in all cases.

### Biotite.

Biotite No. 2136 is from the biotite-granite at the base of El Capitan in Yosemite Valley. It is quite black in color, as seen with a hand lens, but under the microscope is brown. This biotite-granite forms large areas in the granitic complex of the Sierra Nevada, and is quite uniform in appearance and composition at nearly all points where I have seen it. The biotite which it everywhere contains as an essential constituent, is quite the same in color and degree of pléochroism in the many thin sections examined, and the analysis given below may be fairly assumed to represent in general the composition of the biotite of this granite. Biotite-granite 2136 contains quartz> plagioclase>orthoclase> biotite> magnetite> titanite> apatite >zircon, the last four minerals being merely accessories. The aplitic granites that cut the other granites in dikes likewise contain a very similar biotite in small amount.

A microscopic examination of the material analyzed, as well as the mere fact that phosphorus pentoxide is present, showed that there were apatite prisms mixed with the biotite. The analysis was therefore recalculated and the  $P_2O_6$  (·20) taken out together with the CaO (·26) required by the  $P_2O_6$  (·20) taken out together  $H_2O$  below 110° C. is likewise left out in this recalculation since it was no doubt adventitious.

Biotite No. 1751 S.N. is from a quartz-monzonite collected about 1 klm. southwest of Blood's Station, Alpine County, in the Big Trees quadrangle. The material analyzed was found, on microscopic examination, to contain occasional white grains,

\* Published by permission of the Director of the U.S. Geological Survey.

	Biotite 2136.	2136 recalculated.	Biotite- granite 21.36.	Biotite 1751.	Quartz- monzouite 1751.	Biotite 1743.	Gneiss 1743.	Biotite 2652 S.N.
SiO <sub>2</sub> TiO,	35 64 1 · 1 2	36.02 1.13	80-14	35 62 2-61	16.99	36.62 3-03	51.5	35-75 3-16
$ m ZrO_2$			80.					none
Al203	18-62	18.81	15-90	15-24		14.37		14.70
0r <sub>3</sub> 0 <sub>5</sub>	, , , , ,	1 1 1 1 1 1		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				trace
V 2US		E.G.O				4.04	80.	40. 20 1
FeO	14.60	1475	1.31	4 02		17-09		$^{\pm}0.9$ 14.08
MnO	62.	•80	·15	-74		-40		-45
NiO and CoO								.02
CaO	06.	<u>9</u> 9.	2.60	·95	3.51	1.48		11.
Sr0	none	none	·02	trace		trace		\$
Ba0	trace	trace	•04	-26		•33		$\cdot 12$
Mg0	972	982	·54	12.70	1	89.6		12.37
K <sub>2</sub> 0	9-22	9.32	4.08	7-72	3.13	8-20		9.19
Na <sub>2</sub> 0	•38	98;	3.54	.50	3.59	-45		9 . 99
Li <sub>2</sub> 0	trace	trace	trace	trace	trace	trace		ر عد
H <sub>2</sub> O below 110° C	.48		none	Ŧ6:		06.		1.03*
H <sub>2</sub> O above 110° C	2.54	2.57	•30	4.36		3-26		3.64*
P <sub>2</sub> O <sub>5</sub>	•20		·10	none	8	none		•03
SO3			none		1 1 1 1 1			
	-26	-26	-02 CO <sub>a</sub> trace	none		01.		41.
			000000000000000000000000000000000000000		1	74	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
Total	100-01 11-	100-11 -11	100 60	100-00		99-95 -04		10. 06-66
	06-66	100.00		100.00		16-66		99.83
Analyst	Valentine		Valentine	Valentine	Stokes	Valentine	Hillebrand	Hillebrand
		¶ *	etermined at ]	105° C.				

Analyses of Biotite, and the containing rocks.

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probably feldspar. The impurities, however, form such a minute portion of the material that the analysis may be considered as sufficiently correct for use in calculating the constituents of the granitic rock of which it forms a part. The mica is quite black in color, as seen with a hand lens. Under the microscope it is a darker brown than the biotite of the biotite-granite. This biotite is characteristic of the granodiorite and quartz-diorite series, and of the quartz-monzonite. It contains more magnesia than any other of the biotites analyzed but nearly the same as amphibole 2652, also from quartz-mon-Dr. Hillebrand examined specimen 1751 and the zonite. biotite from it for vanadium. He found that the rock contained .012 per cent of V<sub>2</sub>O<sub>3</sub> and the biotite .066 per cent. Quartz-monzonite 1751 is composed of plagioclase>quartz> orthoclase>biotite>amphibole. There are present as accessories titanite, apatite, and iron ore.

Biotite No. 1743 S.N. is from a pyroxenic gneiss from the south bank of the North Mokelumne River, about 1 klm. up stream from the mouth of Bear River, in the Big Trees quadrangle. The material analyzed was found, on microscopic examination, to contain occasional grains of amphibole, but these probably do not sensibly affect the result. This biotite is reddish-brown in color and quite similar to the biotite so often found in contact metamorphic rocks. Dr. Hillebrand subsequently tested the material for vanadium and found gneiss 1743 contained '08 per cent  $V_2O_3$ , and the biotite from it '127 per cent. Gneiss 1743 is composed of plagioclase, reddish-brown biotite, greenish-brown amphibole, quartz, pyroxene, titanite, magnetite, apatite, and pyrrhotite, the relative abundance being approximately indicated by the order in which the constituents are enumerated.

Biotite No. 2652 is from a quartz-monzonite from a block by the Tioga road southeast of Mt. Hoffmann in the Mt. Dana quadrangle. The amphibole 2652 analyzed is from the same block, and both were separated as well as analyzed by Dr. Hillebrand. The block above referred to was far richer in amphibole and biotite than is usually the case with the quartzmonzonite of the region. There is thus a possibility that these minerals may differ somewhat in composition from the same minerals where they occur evenly distributed through the magma. An examination of the powder analyzed shows on one slide a very few foreign particles, namely, apatite and amphibole. The apatite should of course be deducted from the analysis as well as the water below 105° C. Dr. Hillebrand found that the mica contains no rare earth, zinc, or metals of the H<sub>2</sub>S group. The specific gravity of biotite 2652 at 21° C. is 3.05. Quartz-monzonite 2652 was not analyzed, but for

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purposes of comparison No. 2179, given in the table of amphibole analyses, may be substituted, as this is from the same area and represents the average rock.

A comparison of the biotite analyses given in the table with those of the rocks from which the micas were obtained, does not suggest any very definite relations. These micas are all quite similar in composition. It may be noted, however, that the biotite richest in alumina and alkali is from the most acid rock of the series, the biotite-granite (No. 2136). This rock contains no amphibole. Biotites 1751 and 2652 are richer in magnesia. Both of these are very similar in composition as well as in color and pleochroism, and both of them are assoeiated with amphibole.

	Amphibole 1970	Gabbro 1970.	Amphibole 2652.	Quartz- monzonite 2199.	Amphibole Donegal granite.	Donegal granite.
SiO	46.08	47.27	47.49	66.83	47.25	58.04
TiO	.77	.92	1.21	•54		
ZrO <sub>2</sub>			none	•04		
Al <sub>2</sub> O <sub>3</sub>	10.26	20.85	7.07	15.24	5.65	16.08
Cr <sub>2</sub> O <sub>3</sub>		faint trace*				
V <sub>2</sub> O <sub>3</sub>		.02	·04			
Fe <sub>2</sub> O <sub>5</sub>	2.81	1.82	4.88	2.73	19.11	8.27
Fe0	8.30	4.26	10.69	1.66	•94	0.42
Mn0	·15	trace	.21	•10	1.70	1.12
NiO and CoO		none	02			
CaO	. 12.64	13.02	11.92	3.29	11.76	6.52
Sr0	none	trace	none	·03		
Ba0	none	none	none	.11		
Mg0	14.40	6.44	13.06	1.63	11.26	2.94
K20	•34	·22	•49	4.46	1.04	2.21
Na <sub>2</sub> 0	1.62	2 75	.75	3 10	.98	4.65
Li <sub>2</sub> O	none	none	trace	trace		
H <sub>2</sub> O below 110° C	.12	.08	4	none		
H <sub>2</sub> O above 110° C	1.97	1.27	1.86	:56		
P <sub>2</sub> O <sub>3</sub>	·18	.74	none	·18		
CO2		none		trace		
FeS2		·20				
SO3				none		
Cl		trace		·02		
F	none		.06			
Total	99.99	99.86	100.05	100.82	99.69	100.28
Analyst	Valentine	Stokes	Hillebrand	Valentine	Haughton	Haughton.

Analyses of Amphibole and the containing rocks.

An examination of the powder of amphibole 1970 shows that it contains a few grains of labradorite but otherwise appears

\*  $Cr_2O_3$  and  $V_2O_3$  determined by Dr. Hillebrand.

+ Dried at 105° C. before analyzing. No rare earths or zinc present.

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to be quite pure. The phosphorus pentoxide  $(P_2O_s)$  shown in the analysis must, however, be ascribed to apatite, and this should be deducted from the amphibole analysis together with a corresponding amount of lime. In addition minute black grains may be noted in the amphibole itself. These are probably magnetite, but the amount thus included must be small, since the powder was treated with an electro-magnet and the more highly magnetic grains removed. No titanite or other titaniferous mineral were found in the thin sections of gabbro 1970 or in the amphibole powder. The titanic oxide (TiO<sub>2</sub>) shown in the analysis therefore probably belongs to the amphibole. The pleochroism is strong in brown and greenish brown colors with large extinction angle.

Amphibole-gabbro 1970 is from Beaver Creek about 18 klm. east of Big Trees P. O. in the Big Trees quadrangle. It is composed chiefly of labradorite and amphibole but contains a little pyrite and pyrrhotite.

Amphibole 2652 is exceptionally pure. It is pleochroic in dark green tints with large extinction angle. There are some minute black grains included in the amphibole. These are probably magnetite. One foreign particle only was noted in a slide of the powder. As before stated, this amphibole comes from the same block of quartz-monzonite as biotite 2652. The specific gravity of amphibole 2652 at 21.5° C. is 3.203. Analysis 2179 is that of an average quartz-monzonite of the region. It is well known that the metasilicates of rocks rich in alkalies are sometimes themselves rich in alkali. This relation does not appear to obtain in the case of amphiboles 1970 and 2652, the former of which comes from a basic rock poor in alkali, and the latter from an acid rock rather rich in alkali, yet there is more alkali in the amphibole from the basic than in that from the acid rock.

There is also added to the table an analysis of an amphibole from the Donegal granite<sup>\*\*</sup> as well as one of the granite itself. It is evident from the analysis of this granite that the rock is really a quartz-diorite or granodiorite and not a true granite. The biotite from the Donegal granite is remarkable for the very high content of ferric iron—19·11 per cent.

\* Haughton, Quart. Jour. Geol. Soc. Lond., vol. xviii, 1862, p. 416.

# ART. XXXII.—On one little known and one hitherto unknown species of Saurocephalus; by O. P. HAY.

THE fish Saurocephalus lanciformis was first described and named by Dr. Richard Harlan in 1824.\* This description and the accompanying figures were reprinted in 1835 in the same author's Medical and Physical Researches.<sup>+</sup> The specimen on which the genus and species were based had been collected about twenty years previously, by Lewis and Clark, at some locality probably in northeastern Nebraska. It consisted of the greater portion of the left maxilla; but was described by Harlan as belonging to the lower jaw. He also regarded it as having belonged to a reptile allied to Ichthyosaurus. Louis Agassiz first recognized the ichthyic nature of the remains; (although he confounded them with an entirely distinct species); and his conclusions were confirmed by Richard Owen.§ Dr. Leidy corrected Agassiz's errors, and gave more accurate descriptions and figures of the maxillary than had been furnished by Harlan.

No remains of Harlan's species, other than the maxillary referred to, have hitherto been described. Dr. E. W. Hilgard¶ has reported the species as occurring in the Vicksburg group of the Eocene, but the identification was undoubtedly erroneous. Dr. William Spillman\*\* has also included this species in his list of fossils belonging to the Tombigbee greensand of the Cretaceous at Columbus, Miss. Although this identification is less improbable than the former, we have nothing to confirm its correctness.

Notwithstanding the scantiness of the material belonging to the type species, our knowledge of the genus Saurocephalus has been greatly increased through the descriptions of closely related and more perfectly preserved species. For this additional knowledge we are indebted to Cope and Newton, and more recently to Alban Stewart, of the University of Kansas.

For some time I have had in my possession some remains which on examination prove, in my judgment, to belong to Harlan's species. This material was collected for me in the region of Butte Creek cañon, south of Wallace, Kan.; and the horizon is undoubtedly that of the Niobrara Cretaceous. My material consists of both the mandibles, the right maxilla, the pterygo-palatine arch and a few other bones.

The maxillary (fig. 1) is rather short and deep. The portion belonging in front of the palatine condyle is missing; but the condyle itself is present. The alveolar border is somewhat

<sup>\*</sup> Jour. Acad. Nat. Sci. Phila. [1], iii, pp. 331-337, pl. xii, figs. 1-5.
† Med. Phys. Res., pp. 362-366, pl., figs. 1-5.
‡ Poiss. Foss., v. p. 102.
[Trans. Amer. Philos. Soc., 1857, xi, pp. 91-95, pl. vi, figs. 8-11.
¶ Report Geol. and Agric. Mississippi, 1860, p. 142.

# O. P. Hay—Species of Saurocephalus.

curved, and is occupied by compressed sharp-edged teeth. Of these there are present twenty-eight; but if we restore the bone, as we can safely do, I believe, by aid of Stewart's figures



of S. dentatus,\* we may conclude that there were originally thirty-four teeth, possibly one or two less. The root of the most anterior tooth has been exposed by the fracture, and its fang is seen to be distinctly faceted; so that it presents just such an appearance as the tooth of S. lanciformis figured by Leidy.† The roots of teeth situated more posteriorly whose fangs have been exposed by a tool are similarly faceted. Cope states‡ that S. lanciformis is to be distinguished from his S. arapahovius, by the lack of facets on the roots of the teeth of the latter.

Leidy estimated that the maxilla in his hands had supported only twenty-six or twenty-eight teeth, and he was probably correct. That maxilla, a larger one than the one in my possession, seems to have been broken just behind the palatine condyle. If now we take from Leidy's drawing the width of the bone at this point and apply it to the alveolar border, we find that it includes ten teeth; the width of my own specimen includes thirteen teeth. It is not impossible, however, that the specimen figured by Leidy had been broken away some little distance behind the condyle. At any rate, I do not believe that the difference of a few teeth, other things being alike, would justify us in regarding the specimens as belonging to different species.

As in the case of the original specimen there is a shallow groove running along the mesial surface of the maxilla, about  $5^{mm}$  from the alveolar border, and from this groove foramina, one for each tooth, enter the bone.

Depth of maxillary at palatine condyle ..... 38<sup>mm</sup> Distance from anterior end of palatine condyle

to hinder end of maxillary ...... 85mm

The right mandible is shown in fig. 2, five-eighths the natural size and showing the mesial surface. The alveolar border is straight and supports thirty-four teeth, of which those occupying the middle of the border are the largest. In general, they are larger than the teeth of the upper jaw. The line

\* Kan. Univ. Quart., vii, p. 25, pl. i, figs. 3a, 4a.

+ Trans. Amer. Philos. Soc., xi, pl. vi, fig. 9. ‡ Cretaceous Vertebrata, p. 216.

which spans thirteen teeth in the maxilla spans ten in the dentary. At the proximal end of the mandible there must have been a process of the dermarticulare, as in related forms; but in the specimen figured it is hidden by the overlying



ceratohyal, which is not shown in the figure. At the anterior end of the mesial face of the dentary there is found a broad surface, rough with processes and pits, an indication that the two dentaries were strongly bound together. The extreme anterior end of each dentary is occupied by a surface to which was evidently attached such a predentary as Stewart has described as belonging to several related species. A groove and a row of foramina are present on the median face of the dentary.

> Length of alveolar border ...... 112<sup>mm</sup> Length of mandible from cotylus... 130 Depth of mandible at last tooth.... 56 Depth of mandible at symphysis ... 34

Fig. 3 represents, five-eighths the natural size, the pterygopalatine arch seen from within. A triangular piece is missing from the anterior end, and the lower end of the ectopterygoid,



pg, is defective. As I interpret the bones, the arch is remarkable for the large size of the palatine, pa. While the sutures which are represented in the figure are very distinct, I am wholly unable to find one separating the entopterygoid, ep, from the metopterygoid mt. pg. On the upper border of the

arch, at the point indicated by the line s, there appears to be an indication of a suture. If such it is, it probably extends downwards to a point near the hinder end of the palatine. The arrangement of the bones is quite different from that found by myself in *Xiphactinus*.\*

At the lower border of the anterior end of the palatine there is a broad surface, v, which was probably in contact with an articulating surface on the vomer. The notch seen in the anterior end is occupied by another articulatory surface, mx, for the anterior palatine condyle of the maxilla. The anterior end of the upper border furnished an articulation, pfc, with the prefrontal, but this is elongated and rough, not broad and smooth, as it is in Xiphactinus.

Anteriorly the palatine is thick and strong. On its outer surface this portion is finely vermiculated above, while the lower portion furnishes a concave articulation for the condyle of the maxilla. The general appearance of this portion may be seen from fig. 4, which represents the palatine of the next species. Below the concave surface for the palatine condyle of the maxilla there is seen a broad rough surface which must have been applied to the inner face of the maxilla. The greater portion of this is wanting in the specimen shown in fig. 4. Its limits are indicated by the dotted line. On the outer face of the metapterygoid, from the highest point seen in fig. 3 there runs downward and backward a sharp ridge which evidently bounded the orbit below. The portion of the metapterygoid above and mesiad of this ridge formed the floor of the orbit. This indicates that the orbit was placed well backward. I find no satisfactory evidences of the presence of teeth on the pterygoid and palatine bones. If we shall add to the maxillary the probable antero-posterior extent of the premaxillary, we shall find that it is approximately equal to the length of the lower jaw. Hence the latter did not project beyond the upper jaw as it did in the case of those species which Stewart has referred to the genus Saurodon.

Two characters seem to distinguish Saurodon from Saurocephalus, viz.: the presence of notches, instead of foramina, for the successional teeth and the projection of the lower jaw beyond the snout of the fish. I have been inclined to believe that the presence of these two characters is sufficient to distinguish Saurodon as distinct. However, I observe in some specimens of this supposed genus that some of the notches become closed into foramina; and we can easily imagine all gradations between notches and foramina high above the alveolar margin. Moreover, it is probable that the other character will fail. Recently Mr. Stewart<sup>+</sup> has published figures, without description, of remains which he refers to Cope's Sauro-

\* Zoolog. Bull., ii, 1898, p. 39, fig. 7.

+ Kan. Univ. Quart., vii, pl. xvi, figs. 4, 5.

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don phlebotomus. Mandible and maxilla are shown. Measurements show that the maxilla, without the premaxillary, is nearly as long as the alveolar border of the mandible, so that it is almost certain that in this species there was no projection of the dentary beyond the snout. It seems probable therefore that Saurodon must be abandoned.

I present here (fig. 5) the right maxilla and the premaxillary (fig. 4) of another species of *Saurocephalus*, which I regard as yet undescribed. It is especially distinguished from described species by its elongated maxillary bone. To illustrate this, I compare it with Mr. Stewart's *S. dentatus*, which is itself a species with a rather long maxilla. In *S. dentatus* the total



length of the maxilla is  $142^{\text{mm}}$ , its height at the palatine condyle  $45.5^{\text{mm}}$ . My specimen has the same height at the condyle; but the total length is  $172^{\text{mm}}$ , a difference of  $30^{\text{mm}}$ , equal to 21 per cent of the shorter maxilla. My species, therefore, probably had a relatively slender head and a larger mouth than had *S. dentatus.* 

In the maxilla figured I count alveoli for thirty-seven teeth; but in the maxilla of the other side, somewhat broken, the teeth extend backward somewhat farther; so that there must have been forty. At some time in the career of its owner the right maxilla has been fractured obliquely across its middle, and this accident has affected the neighboring teeth. One of these has thus become exposed nearly half-way to the tip of the fang. This exposure reveals the fact that the fang is faceted, as it is in *S. lanciformis*. The great length of the maxilla distinguishes this species from both *S. lanciformis* and *S. dentatus*, and the facets on the teeth distinguish it from Cope's *S. arapahovius*. Mr. Stewart has not described the condition of the fang of the teeth of his *S. dentatus*.

In fig. 5 p. c represents the palatine condyle; p. c', the anterior palatine condyle which was applied to a surface like that shown in figure 3 at inx.

I propose to call the fish above described Saurocephalus pamphagus.\*

\* Inde ruunt alii rapida velocius aura, Pamphagus et . . . . . .

Ovid, Met., Bk. iii, l. 209.

It has been supposed that the foramina, situated one opposite each tooth and on the mesial face of the maxilla and of the dentary, are for the transmission of nerves and vessels to the teeth. Richard Owen\* seems not to have so regarded these foramina. He believed that they "lead to the cavities containing the germs of the successional teeth." The latter probably began their development in, or at the bottom of, these foramina; but they soon passed more deeply into the bone. In fig. 1 at tthere is found a developing tooth whose tip is on a level with the row of foramina; but its root extends high up into the bone. Nerves and vessels entering the tooth by way of the foramina alluded to would have to take a very tortuous course. The functional tooth immediately below the young tooth figured seems already to have suffered some reduction of its fang.

The germs of the teeth of the Saurocephalidæ did not gain a lodgment in the bones of the jaws in the same way that the teeth of the higher vertebrates did. In the latter the fangs were first planted in grooves in the dental borders of the bones; and we must suppose that these grooves, at first shallow, have, in successive generations, deepened and become portioned off to form sockets. In the Saurocephalidæ the teeth, developing originally on the dental border, have gradually migrated away from this border, on the mesial face of the supporting bones, and, by means of the foramina described above, have made their way through the mesial wall of the sockets. The notches found in the species referred to Saurodon show the earliest stages of this migration.

The distinguished palae-ichthyologist, Mr. A. S. Woodward, has recently kindly called my attention to a suggestion made by Prof. E. D. Cope that the Saurocephalidæ are closely related to the Chirocentrida, represented by the large Chirocentrus dorab of the Chinese and Indian seas. I have unfortunately had no opportunity to study a skeleton of this fish; but, judging from the figures of the fish found in Cuvier and Valenciennes, pl. 565, and in Day's Fishes of India, pl. clxvi, fig. 3, its external appearance must be much like that of the extinct Xiphactinus. Nevertheless, we have no intimations that the teeth of *Chirocentrus* are fixed to the jaws in any way different from those of ordinary fishes. The fixation of the teeth in sockets is an unusual thing among fishes; and this character alone, it appears to me, is sufficient to remove Xiphactinus and its allies from the Chirocentridæ, although not necessarily to a great distance. I suspect that the Saurocephalidæ will, when they are better known, show distinctive characters in the vertebral column also.

\* Odontography, p. 131.

# ART. XXXIII.—A Study of Some American Fossil Cycads. Part II. The Leaf Structure of Cycadeoidea; by G. R. WIELAND. (With Plate VII.)

### Introduction.

It is generally conceded that the Cycads culminated in the Jurassic, and formed the principal plant life of that time. Nevertheless, the abundant and widely distributed fossil remains of this vegetation consist almost entirely of disconnected and scattered trunks, leaves, and occasional fruits, which have been described under separate generic and specific names. So uniformly is this true that Count Solms-Laubach<sup>\*\*</sup> mentions an individual of Zamites gigas, Morr., from the upper Jurassic sandstone of Yorkshire, England, as the only cycad known to him, whose stem with the leaves attached may be identified with certainty. This specimen, now in the Paris Museum, is figured by Saporta,<sup>\*</sup> and in leaf and habit is said to recall Stangeria most nearly.

There has, therefore, been no sufficient means of correlating the various genera and species founded on isolated parts,—a fact which now makes especially important a determination of both trunk and leaf characters when united in a single individual. For this reason it is fortunate that not only the leaf and its prefoliation, but also the accompanying floral characters, may be completely determined in a number of the unusually perfect cycadean trunks now in the Yale collection, though but a single one is considered in this paper.

# Prefoliation of Cycadeoidea.

The subject of the present, as well as of the preceding, preliminary study is afforded by the type specimen of *Cycadeoidea ingens*, Ward, a photograph of which has been already given. As previously mentioned, this fine male trunk bears on its summit, above the series of flower buds, a crown of young leaves imbedded in fine scales, or ramentum. It would seem that, having formed its blossoms, this cycad was again preparing to put forth its energies in the unfolding of an additional series of leaves, about twenty in number. Happening to be fossilized at such a critical time in its life, under the most favorable conditions, there has been preserved a wealth of characters scarcely equalled by any Mesozoic plant of which there is a record. This specimen alone affords all the material required for a restoration.

\* The numbers refer to the list of papers given in Part I of these studies. This Journal, March, 1899, pp. 219-226, Plates III, IV. A careful examination of the summit of the trunk showed that, as found in the field, it had been subjected to the erosive action of sand-laden winds which had partially exposed several transverse sections of the tips of young leaves. It was found that these belonged to a circularly placed series just ready to emerge at a distance of from 5 to 8 cm from the apex. Several pairs of these leaves enveloped in ramentum were removed for study, and the disposition of their parts with reference to the trunk determined from longitudinal, transverse, and tangential sections.

As so removed, each rachis with its attached pinnules formed an erect subcylindrical, or spindle-shaped, body, 6 cm in length, with a long diameter of 15 mm coinciding with the radius of the trunk, and a short diameter of 12 mm at right angles to it. The rachis was erect and situated distally on the long diameter. It bore the pinnules inclined inwards in two imbricating ranks, formed by the two rows of pinnæ on each leaf, in such manner that their upper surfaces all faced towards the axis of the trunk.

A clearer perception of the arrangement of the pinnules with respect to the rachis and the trunk may be had if an ordinary, expanded, young Zamia leaf is considered in its natural position on the summit of the trunk. If the pinnules of such a leaf are folded toward the axis of the trunk in two ranks, and these ranks are brought together side by side, the position of the parts in the unexpanded young leaf of *Cycade*oidea will be paralleled. As just stated, it at once becomes apparent that the rachis is farthest away from the trunk, and that the upper side of each pinnule faces the axis of the trunk. This is also the relative position of the parts in the unexpanded young leaf of Zamia. Cycadeoidea thus had the direct mode of prefoliation characterizing the existing North American eyeads Zamia and Dioön.

# The Cycadeoidean Leaf Structure.

While an exhaustive treatment of the anatomy of these leaves must be deferred for the present, the features of more immediate interest may be here described.

The exact arrangement of the pinnules and of their fibrovascular bundles is shown in the transverse section, figure 2 (Plate VII), and in the longitudinal section, figure 3, the general position of these sections being indicated in figure 1.

The transverse section, figure 2, shows that, just above the termination of the rachis, there are 20 pairs of projecting pinnules. Since the pinnules nearest the rachis must necessarily

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be cut through their bases, while in a given transverse section those farthest from the rachis must be cut through their tips (as may be understood by referring to figure 1), this transverse section virtually represents a series of sections such as would be obtained if a single pinnule were cut transversely 20 times at regular intervals from base to tip. Nearer the base of the leaf, a transverse section cuts 34 pinnules. As there are about 20 insertions of pinnules above this basal section, and apparently no pinnules lying wholly beneath it, there are approximately 60 pinnules in all. The rachis and pinnular insertion have not yet been studied.

The principal fact of interest shown by the longitudinal section represented in figure 3 is the emergence of leaf tips on the side next the axis, or rachis, of the leaf. As this section is wholly above the termination of the rachis, this emergence indicates that the topmost pinnæ are relatively short. Necessarily, then, the leaf at this stage of its growth was of a somewhat truncate form.

This fact, however, does not permit surmise as to the exact leaf habit of *Cycadeoidea*, for subsequent growth either may have increased the truncation, or, because of great elongation of the rachis, resulted in a lanceolate leaf. Presumably the study of the prefoliation and subsequent development of the rachis and pinnæ of living cycads, especially *Zamia*, will indicate what must have been the appearance of the full-grown leaf of *Cycadeoidea*.

The microscopic structure of the pinnules is partially shown in figures 4 and 5. In figure 4 is shown a transverse section through a pinnule cutting a fibro-vascular bundle. The structure of the relatively heavy epidermis of the upper side of the pinnule is not distinct even in this young stage, and forecasts a dense and stiff structure. A single layer of sclerenchyma cells of rounded section forms the hypodermis, from which a double row of similar cells passes in confluently to the bundle, where it divides to form a more or less complete circular row of sclerenchyma cells enclosing the phloem and xylem. The uniformity of this arrangement gives the transverse section of the bundles a characteristic flask-shape. Beneath the hypodermis is a distinct layer of palisade parenchyma followed by an indistinct one grading into the rounded parenchyma cells occupying the space between the bundles. The lower portion of the leaf, or that beyond the bundles, is composed of welldefined spongy parenchyma, with distinct intercellular spaces, and is bounded by a thin epidermis, the structure of which is not well marked. The lower surface at this stage is somewhat glabrous, although revolute margins are apparently indicated.

In figure 5 is shown a longitudinal section through the palisade parenchyma and bundle connection, with the hypodermis. This section displays clearly the usual dichotomous cycadean venation, as well as the mode of bundle increase. The pinnæ are of linear-lanceolate form, and without a distinct midrib.

A comparison of these structures with those of Zamia integrifolia shows a striking resemblance in all essential char-acters,—a resemblance that is even more marked than is that between the pinnæ of Zamia and of some of the other existing genera of the Zamiacea (Zamia).

The character of the ramentum surrounding these leaves remains to be briefly mentioned. It consists of thin scales, or hairlike forms, composed of stringy elements, and strongly resembles the ramental cells figured by Carruthers' and Seward's in their respective descriptions of Bennettites Gibsonianus and Cycadeoidea gigantea. A transverse section of the ramentum is shown in figure 6. The flat sides of these scales quite uniformly face the leaves, though as such a large portion of the summit is occupied by a mat of relatively the same character, it is probable that much of this hairy and scaly material is borne on the trunk in the space intervening between the petioles of the young leaves.

Yale Museum, New Haven, Conn., March 20, 1899.

### EXPLANATION OF PLATE VII.

FIGURE 1.-Diagram of a hypothetical leaf, with a reduced number of pinnules, showing the position of the sections represented in figures 2 and 3. O, O', are in the plane of the transverse section, figure 2, and also

FIGURE 2.—Cycadeoidea ingens, Ward (type); transverse section floure 3.
 FIGURE 2.—Cycadeoidea ingens, Ward (type); transverse section through upper portion of young leaf. × 4. For relative position, see figure 1.
 a, upper side of an inner pinnule cut near the summit; b, fibrovasulas hundhe, a viewnle with the summit; b, fibrovasulas hundhe.

vascular bundle; c, pinnule cut near the base; d, axis of growth of rachis. The arrows indicate approximately the base line O, O', figure 3.

FIGURE 3.-The same specimen; longitudinal section through summit of young

leaf. × 4. For relative position, see figure 1.
 a, summit of a pinnule near apex of leaf; b, upper side of pinnule;
 c, base line of section indicated in figure 1, O, O'.
 FIGURE 4.—The same specimen; transverse section through a single pinnule,

showing a fibro-vascular bundle.  $\times$  60.

a, upper side of leaf: b, hypodermis; c, sclerenchyma connection of hypodermis with fibro-vascular bundle; d, palisade parenchyma; e, xylem; f, phloem; g, spongy parenchyma; h, epidermis of under side of leaf.

FIGURE 5 .- The same specimen; longitudinal section through a pinnule just beneath the hypodermis cutting the palisade parenchyma.  $\times 35$ .

a, forking vein; b, palisade parenchyma. FIGURE 6.—The same specimen; transverse section through the ramentum surrounding the young leaves.  $\times 60$ .

# SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. On Luminous and Chemical Energy.-The radical distinction which exists between photochemical reactions which are endothermic, in which light energy is converted into chemical energy, and those which are exothermic, in which the light is merely auxiliary, the greater portion of the change being effected by purely chemical agencies, has been recently emphasized by BERTHELOT, who has pointed out that it is only the former class of reactions which are adapted for use in the measurement of luminous energy. He has studied a number of substances when exposed to direct sunlight, to diffused daylight, or when kept in the dark, with reference to the changes thereby produced. The substances were contained in sealed tubes and the effect of different wave-lengths upon them was determined by surrounding them with colored media. Nitric acid when concentrated is decomposed by light at ordinary temperatures, and possibly at still lower temperatures, the reaction being similar to that which takes place in the dark at 100°, and which yields nitrogen per-oxide, oxygen and water. The blue rays are most effective in producing the action, which is endothermic and not entirely reversible. The diluted acid is not affected by light, that of density 1.365 undergoing no change after weeks of exposure. The nitrogen peroxide formed tends to absorb those rays which are active in producing it. Iodic acid and oxide, while stable in diffused daylight, are decomposed by direct sunlight, setting free iodine and oxygen; the reaction being analogous to that produced by heat at 300°. It is limited by the absorptive action of the iodine vapor and by the deposition of iodine on the surface of the compound. Hence, while endothermic, this reaction is not suitable for the measurement of light energy. The action in the case of hydrogen iodide is on the line limiting endothermic and exothermic reactions, though the author's view is that a small amount of heat (0.4 calory) is evolved; though when solid iodine is set free, it is decidedly exothermic, 6.4 calories being evolved. The blue and violet rays are most effective, and the decomposition is most rapid in direct sunlight, there being an intermediate production of hydrogen periodide (HI, ?). Hydrogen bromide is not affected by the action of light even at 100°. Nor was any action observed with CO, either alone or mixed with hydrogen, with CO alone or mixed with hydrogen or oxygen, with SO, or HNO, when mixed with hydrogen. Red mercuric oxide is more rapidly decomposed than the yellow variety. Mercurous oxide when exposed to light yields traces of metallic mercury. No action was noticed with lead peroxide, silver oxide, or with mercuric chloride, bromide or iodide. Hence the author considers that the measurement of luminous energy by transformation into chemical

energy is to be effected by means of endothermic reactions which are irreversible at ordinary temperatures.— C. R., cxxvii, 143–160, July, 1898. G. F. B.

2. On the Homogeneity of Helium.-By diffusion through a pipe stem, RAMSAY and TRAVERS separated a volume of helium first into six fractions. The first fraction was then pumped into the diffusion vessel, where one-half of it was diffused and transferred to vessel (1). Fraction No. 2 was then added and one-third of the mixture was diffused and transferred to vessel (1). Fraction No. 3 was then added and one-half of the whole diffused and transferred to vessel (2). Fraction No. 4 was then added and one-half diffused and transferred to vessel (3); and so on. Four complete fractionations of this sort in the case of air gave at the extreme fractions 17.37 and 22.03 per cent of oxygen respectively. When nitrogen was thus used, prepared from ammonium chloride and sodium nitrite, thirty fractionations produced no variation in density. In the case of helium, repeated fractionations of the gas from samarskite and cleveite gave a gas of density 1.98 and of refractivity 0.1238 as the lightest fraction and a very little pure argon as the heaviest one. Since further diffusion did not alter the density of the lighter fraction, the authors regard it as pure helium. "It appears therefore that helium contains no unknown gas nor is it possible to separate it by diffusion into any two kinds of gas; all that can be said is that most minerals which evolve helium also evolve argon in small quantity." The authors had hoped to find a gas with density 10 and atomic mass 20; since this would form with He = 4 and A = 40 a triad like that of F, Cl and Mn, 19:35.5:55. They still regard the existence of such an element as probable.-Proc. Roy. Soc., lxii, 316-324, January, 1898. G. F. B.

3. On the Properties of Ozone.-By means of liquid air, LADEN-BURG has condensed ozonized oxygen to a liquid. Then by allowing this to evaporate partially, he has obtained a residue much richer in ozone, since this gas is less volatile than oxygen. So that by repeating the operation, he obtained finally a gas which contained 86.16 per cent of ozone and which had a density of 1.3698 as compared with oxygen, this density being determined from the rate of diffusion. Hence it follows that the density of pure ozone would be 1.456, theory assigning to it 1.5. He finds that ozone is not as soluble in water as has been supposed, 0.01 volume only being absorbed at the ordinary temperature and pressure, or 0.00002 part by weight. By condensing ozonized oxygen, allowing the oxygen to evaporate and then ascertaining the temperature at which the residual ozone evaporated, an attempt was made to determine the boiling point of ozone. The oxygen volatilized at -186°, leaving 4 or 5°° of an almost black opaque liquid, the temperature of which then rose to -125°, at which point the liquid exploded. This temperature therefore can be taken only as a lower limit.-Ber. Berl. Chem. Ges., xxxi, 2508-2515, October, 1898. G. F. B.

4. On the Preparation of Alkali Nitrites.-It has been pointed out by DIVERS that the common impression that in preparing alkali nitrites by passing nitrous fumes into alkali solutions, a method proposed by Fritsche in 1840, there is also produced much nitrate, is erroneous. The nitrous gases are made from nitric acid and starch or arsenous oxide, and are passed into the concentrated solution of the hydrate or carbonate until neutrali-zation is effected; the vessel being loosely stoppered. The strength of the acid and the temperature are so regulated that the nitrogen monoxide is in excess of the dioxide. If the solution is acid, it must be boiled until neutral before exposing it to the air. Then the solution may be freely evaporated to crystallization. Both potassium and sodium nitrites are slightly yellow in color and are slightly alkaline. Sodium nitrite fuses at  $271^{\circ}$  and at 15° five parts of it requires six parts of water to dissolve it. It is moderately deliquescent, and its crystals are anhydrous. Potassium nitrite is very deliquescent, is soluble in about onethird its weight of water, and its crystals are reputed to contain half a molecule of water. -J. Chem. Soc., lxxv, 85, January, 1899. G. F. B.

5. On the Composition of American Petroleum.-By means of a combined dephlegmator and regulated temperature still-head, Young has succeeded in preparing from American petroleum ether a number of nearly pure hydrocarbons. In some cases the fractional distillation was preceded by treatment with mixed nitric and sulphuric acids, in order to remove the benzene. Evidence of the presence of the following has been thus obtained: Isopentane B. P. 27.95°, normal pentane B. P. 36.3°, penta-methylene B. P. about 59°, isohexane B. P. about 61°, normal hexane B. P. 68.95°, methylpentamethylene B. P. about 72°, benzene B. P. 80.02°, hexamethylene B. P. 80.8°, isoheptane B. P. 90.3°, dimethylpentamethylene (?) B. P. about 94°, normal heptane B. P. 98.4°, methylhexamethylene B. P. about  $102^{\circ}$  and toluene B. P. 110.8°. These results show that the same classes of hydrocarbons, paraffins, polymethylene compounds or naphthenes and aromatic hydrocarbons are present in petroleum from all three sources, but that Russian petroleum contains a relatively larger amount of naphthenes and in all probability, of aromatic hydrocarbons than Galician, and Galician a larger amount of the same hydrocarbons than American petroleum.-J. Chem. Soc., lxxiii, 905-920, December, 1898. G. F. B.

6. Electrical waves along wires.—A. SOMMERFELD has examined by means of elaborate mathematical analysis this subject, and has calculated the rate of damping and the decrease of velocity for the case of wires of different diameters. In the case of a copper wire  $4^{mm}$  thick with a period of 10° per second, the electric wave velocity was 8 kilometers below the velocity of light. With a platinum wire of  $\frac{4}{10} \sigma_{1}^{mm}$  diameter, period 3:10° per second, the velocity falls to  $\frac{3}{4}$  of the velocity of light. The ordinary experimental method, in which two parallel wires are used, offers great mathematical difficulties. The author is apparently unacquainted with the direct experimental determination of the velocity of electric waves by Professor Trowbridge and Professor Duane, which avoids the mathematical difficulties, and by which a velocity closely agreeing with that of light was obtained.— *Wied. Ann.*, No. 2, 1899, pp. 233-290. J. T.

7. Polarization and hysteresis in dielectrics.—W. SCHAUFEL-DERGER employs ellipsoids of paraffine and hard rubber, and studies the damping of their oscillations in the electric field of a Kohlrausch condenser. The mathematical consideration of the motion of the dielectric contains hypotheses drawn from analogous phenomena of polarization and hysteresis in the case of iron. It was found that the loss of energy due to hysteresis in paraffine is 2·119 per cent and in hard rubber 63·49 per cent. The latter number is regarded as an approximation.—Wied. Ann., No. 2, 1899, pp. 307-324.

8. A new method of showing electric waves.—A simple resonator devised by Rhigi consisted in a sheet of tinfoil applied to glass, the foil being divided by a fine line. ALBERT NEUGSCHWENDER has discovered that if a galvanometer and a battery are placed in circuit with a silver-coated surface divided by a fine line, that the galvanometer will show a deflection due to a Hertzian wave if one breathes on the metallic surface or places a wet sponge near it. The vapor converts the divided surface into a species of coherer.— Wied. Ann., No. 2, 1899, pp. 430-432.

9. Separation of long waves of heat by means of quartz prisms.—The very important work of H. RUBENS and E. ASCHKINASS on this subject has shown that it is possible by means of quartz and sylvine to isolate waves of heat of great wave-length, since these waves are not absorbed by these substances. The above authors have now entered into a discussion of the further extension of their method. They find that intensity of energy between wave lengths  $50\mu$  and  $60\mu$  is greater than the whole energy beyond  $\lambda = 60\mu$ . Since the energy between 50 and  $60\mu$  is only  $\frac{1}{100,000}$  of the whole amount of energy emitted by the sources employed by them (Auer burner), it does not appear possible to further extend their method.—Wied. Ann., No. 2, 1899, pp. 459-466. J. T.

10. Theory of conduction of electricity through gases by charged ions.—Professor J. J. THOMSON has reduced his observations upon this subject to a mathematical form, and has obtained equations which embody his experimental results. He explains many of the phenomena observed in Geissler tubes, and believes that the most striking features of the discharge through vacuum tubes are due to the difference in velocity between the positive and uegative ions. He points out that a study of the distribution of intensity in Geissler tubes supports the theory of ionization.— *Phil. Mag.*, March, 1899, pp. 253–268. J. T.

11. The Hall phenomenon and the theory of Lorentz .-- POINCARÉ

J. T.

has applied Lorentz's theory of electrical ions to the Hall phenomenon and has obtained an equation which represents the electromotive force obtained by Hall. He concludes that it would be desirable to examine whether all metals exhibit the Hall effect when they carry currents of very high electromotive force and whether a change of sign occurs.—*Comptes Rendus*, No. 6, Feb., 1899, pp. 339-341. J. T.

12. On the Relation of the Surface Tension and Specific Gravity of certain Aqueous Solutions to their State of Ionization .- Prof. MacGregor has shown that it is possible to calculate the various properties of solutions of potassium and sodium chloride in terms of the state of ionization of the electrolytes contained. The relation derived, in its simplest form, is  $S = S_n + k(1-a)n + lan$ . where S is the numerical value of any property of a solution (density, surface tension, etc.),  $S_{\rm e}$  that of the same property of water under the same physical conditions, n the number of equivalent gram-molecules per unit volume, a the ionization coefficient of the electrolyte in the solution, and l and k constants, called ionization constants, for any given property of any given electrolyte. Mr. E. H. ARCHBALD has carried out a similar series of observations and calculations in the case of simple solutions of sodium, potassium and copper sulphates, salts of more complex molecular structure than those previously examined. He concludes that the expression given represents observed values of the surface tension and specific gravity of the solutions examined through a range of concentration extending from 0.05 to about 0.4 or 0.5 equivalent gram-molecules per liter. Further, that it is possible by aid of the dissociation theory of electrolysis to predict the surface tension and specific gravity of mixtures of potassium and sodium sulphate solutions and the specific gravity of mixtures of solutions of potassium and copper sulphates throughout nearly the same range, within the limits of the error of observation. And similarly, that it is possible to predict the specific gravity of mixtures of solutions of potassium sulphate and sodium chloride.

13. On the Cause of the Absence of Coloration in certain Limpid Natural Waters.—Professor W. SPRING has an interesting article upon this subject in a recent number of the Bibliothèque Universelle (Jan. 15, 1899). Recognizing the accepted fact that pure water is distinctly blue, he remarks that the green color often observed is easily explained as due to the presence of more or less muddiness, which acts with the natural blue color to give a sensation of green. The absence of color, however, is a different problem, as early noted by Berzelius. The results of some experiments have led the author to the hypothesis that the suspension of minute, perhaps invisible, particles of anhydrous ferric oxide, or hematite, would have, through their red color, the effect of neutralizing the blue and leaving the water completely colorless. He notes the fact that microscopic grains of hematite are almost always found distributed in the soil, and that terrestrial waters have rarely the blue color which the pure liquid

AM. JOUR. SCI.-FOURTH SERIES, VOL. VII, No. 40.-APRIL, 1899. 21 should show. On the contrary, the water derived immediately from snow at high altitudes, or from glaciers, contains no hematite and is commonly intensely blue. The action of hydrated ferric oxide is different, since its color is yellow, and when present in very small amounts in the water, there is, so to speak, a strugglebetween it and the organic matter; if not overcome, the effect is to make the water appear green to the eye.

14. A Text-Book of General Physics for the use of Colleges and Scientific Schools; by CHARLES S. HASTINGS and FREDERICK E. BEACH; pp. viii, 768. Boston, 1899 (Ginn & Company) .--The appearance of a new high grade text-book of physics is an event of much importance to all teachers and students in this department. The authors are to be congratulated upon the admirable manner in which they have treated the entire subject, particularly for their success in adequately presenting so vast a range of topics within the limits of a single moderate-sized volume. The work is characterized by the very careful and thorough treatment of the fundamental conceptions of the science; by the well-balanced relation between the different parts, no one portion of the subject being sacrificed to another; by the clear and precise mathematical development of each successive principle. At many points, moreover, though dealing with topics often treated of, there is much that is fresh and suggestive; this is particularly true of the chapters on Light.

The conciseness of expression and the mathematical, though elementary, method of presentation adopted have the advantage of brevity and accuracy, but they may leave much for the teacher to do if his pupils are approaching the subject for the first time. The student, however, who is properly prepared, will find no serious difficulty, and his subsequent work in special advanced fields will be much facilitated by the thorough grounding in principles and methods which he has here obtained.

Too much praise cannot be given to the publishers for the admirable form in which they have placed the work before the public. The page is clear and open, with no confused crowding of mathematical expressions, while the excellence of topography, illustrations and paper leaves nothing to be desired.

# II. GEOLOGY AND MINERALOGY.

1. New facts regarding Devonian Fishes. Dentition of Devonian Ptyctodontidea; by C. R. EASTMAN; Am. Nat., vol. xxxii, pp. 473-488 and 545-560. July and August, 1898. Some new points in Dinichthyid Osteology; by C. R. EASTMAN; Am. Nat., vol. xxxii, pp. 747-768. October, 1898.—The first of these papers is the result of study of the rich material from the State Quarry fish-beds discovered by Prof. Calvin in the Devonian of Johnson County, Iowa (see Ann. Rept. Iowa Geol. Survey, vol. vii, 1897); private collections made by Mr. E. E. Teller and C. E. Monroe from the Hamilton limestone quarries of Milwaukee, Wis.; and the Schultze collection in the Museum of Comparative Zoology containing European fish remains. The species described belong to the genera *Ptyctodus* Pander, *Rhynchodus* Newberry, *Palcomylus* Woodward, and ichthyodorulites are described under the new generic names *Phlyctenacanthus* and *Belennacanthus*.

The stratigraphic relations of the fish remains and their association with invertebrate fossils lead the author to agree with the general conclusions of Stuart Weller regarding the relation of the Milwaukee beds to the New York and Iowa faunas.

"The Chimæroids give it (the hydraulic limestone of Milwaukee) a stamp of antiquity, suggesting that a westward migration took place during the early part of the Devonian as far as Wisconsin, but not crossing the Mississippi Valley until the Middle Devonian. The Milwaukee beds show the first traces of the encroachment from the East, the Rock Island locality a somewhat later, and the state quarry limestone the last of all, with its horde of Upper Devonian lung-fishes."

The second paper gives a critical comparative study of the cranial osteology of the Dinichthyids, with a particular description of an early type, *D. pustulosus* Eastman, based upon specimens from the Milwaukee and Iowa localities. The author considers this species to be the most primitive member of the genus known. His studies lead him to regard *Coccosteus* and *Titanichthys* as the extreme limits of the family Coccosteide, with *Dinichthyids* the author says: "But when their characters shall have been fully investigated, the wide range of variation manifested by them will be found reducible to order, and the whole promises to constitute one of the most interesting evolutionary series known among fossil fishes" (p. 747).

H. S. W.

2. Geological Sketch of San Clemente Island; by W. S. T. SMITH. Extr., 18th Ann. Rept., U. S. Geol. Survey, 1896–97, Part II, pp. 459–496, plates lxxxiv-xcvi, figs. 82–85. 1898.—San Clemente is the southernmost island of the "channel islands" off the southern coast of California. The island has been described as a "tilted orographic block" by Lawson. The rocks are chiefly volcanic. The oldest sedimentaries are of Miocene age. The author recognizing this as a typical fault block, and isolated from other land masses, the topography of which is still in its infancy, has presented a theory as to the development of its drainage. He also describes the structural and petrographic features of the volcanics, and a general description of the sedimentaries, moraines and later deposits. H. S. W.

3. Geology of the Edwards plateau and Rio Grande plain, etc.; by ROBERT T. HILL and T. WAYLAND VAUGHAN. Extr., 18th Ann. Rept., U. S. Geol. Survey, 1896-7, Part II; pp. 193-321, plates xxi-lxiv, figs. 53-76. 1898.—The geological features of the region from Austin, Texas, westerly and southwesterly through San Antonio to the Rio Grande, are described and beautifully illustrated in this report. Although it does not attempt to be an exhaustive paper on the statistics and engineering problems incident to developing the water supplies, the geology is presented in its relations to the occurrence of underground waters, their sources and relations to the beds carrying them. The paper not only presents an admirable exposition of geological structure, but must prove of great value in guiding the inhabitants of the region in supplying themselves with large supplies of fresh waters.

H. s. w. 4. South Dakota Geological Survey, Bulletin No. 2; by JAMES E. TODD, State Geologist; pp. 1–139, plates i–xv, figs. 1–2. 1898.—This second bulletin contains the 1st and 2d biennial reports with accompanying papers for the years 1893 to 1896. The papers of chief importance are accounts of the surveys of a Section along Rapid Creek from city westward; A reconnoisance into northwestern South Dakota; The geology along the Burlington and Missouri Railway; and Additional notes on the limits of the main Artesian Basin, i. e., additional to those reported by the U. S. Geological Survey in the 17th and 18th Annual Reports. Numerous detailed sections of the rocks and reproduced photographs of the structure are given. H. s. w.

5. Crater Lake, Oregon; by J. S. DILLER. Extr. Smithsonian Report for 1897, pp. 369-379, plates i-xvi. 1898.—This paper, though a reprint of one which first appeared in the National Geographic Magazine (1897),\* will bear repeating, holding as it does beautiful illustrations of a region of which the author says:

"Aside from its attractive scenic features, Crater Lake affords one of the most interesting and instructive fields for the study of volcanic geology to be found anywhere in the world. Considered in all its aspects, it ranks with the Grand Cañon of the Colorado, the Yosemite Valley, and the Falls of Niagara, and it is interesting to note that a bill has been introduced in Congress to make it a national park for the pleasure and instruction of the people."

н. s. w.

6. International Geological Congress.—The eighth session of the International Geological Congress will be held in Paris in 1900 between the 16th and the 28th of August. The Committee of Organization has announced twenty-two excursions, three of which are general; I, about the Paris Basin; II, Boulonnais and Normandie; III, the volcanic regions of central France. The other nineteen are special local excursions for the study of particular problems. A *livret-guide* will be prepared and ready for distribution the early part of 1900. M. Albert Gaudry, Paris, is the President, and M. Charles Barrois, Lille, is General Secretary of the Committee of Organization. H. S. W.

7. International Geographical Congress.—The Geographical Society of Berlin (Gesellschaft für Erdkunde zu Berlin, F. Baron von Richthofen, Prest., George Kollen, General Secy.) invites the friends and promoters of geography in all countries, and especially

\* See also this Journal for March, 1897.

the members of all geographical societies and cognate scientific bodies or institutes, to assemble at the German capital, Berlin, for the meeting of the seventh International Geographical Congress, to be held from Sept. 28th to Oct. 4th, 1899. Membership tickets may be obtained by gentlemen or ladies by payment of 20 marks to the Treasurer, H. Bütow, 90 Zimmerstrasse, Berlin S. W. All wishing to read papers before the Congress are requested to give notification thereof before April 1st, 1899, and to send the manuscript ready for print not later than June 1st, 1899.

H. S. W.

8. Funafuti.-The January number of Natural Science contains an interesting and popular discussion of the life and geological features of Funafuti as a typical coral atoll, by W. J. SOLLAS. Special interest attaches to this island in consequence of the work which has been done here in boring into the coral rock. The party sent out from England, which was directed by Professor Sollas, unfortunately did not succeed in carrying the boring to any considerable depth. The work, however, was continued in 1897 under the direction of Professor David of the University of Sydney, and this time was entirely successful, the reef being penetrated to a depth of 697 feet. Later, a third party was sent from Sydney, which has carried the boring on to a depth of about 1000 feet. The core obtained by the David party was sent to England and is now in the hands of Professor Judd for investigation, the results of which will be awaited with much The general statement is made, however, that the interest. material brought up from the boring, of which the reef is composed, presents much the same character throughout, and so far is regarded as supporting Darwin's theory. There are no layers of chalky ooze, such as Murray's hypothesis might have made probable, and no trace of volcanic material was found. The later boring beyond 700 feet has passed through a hard limestone, containing many well-preserved corals. The last mentioned expedition has also carried on a boring into the bed of the lagoon to a depth of 144 feet. After passing through 101 feet of water, the first 80 feet below were found to consist of the calcareous alga Halimeda, mixed with shells; the remaining 64 feet, of the same

material mixed with coral gravel. 9. Petrographical and Geological Investigations of certain Transvaal Norites, Gabbros, and Pyroxenites; by J. A. LEO HENDERSON (8° pamph., 56 pp., 5 pl., Dulau & Co., Pub., London, 1898).—Although this appears as a separate work, one is led to infer that it is a thesis presented for the doctor's degree at Leipzig. The material upon which the investigations have been carried is from the Stelzner collection at Freiberg and was gathered by the explorers Mohr and Goerz. As may be inferred, therefore, it is a minute and painstaking petrographical and chemical investigation of a series of hand specimens determined as diallage norite, hypersthene norite, hypersthene diallage gabbro, quartz norite, quartz diallage notite and enstatite pyroxenite.

In addition some gneisses and other rocks are described. Among them is a syenite and syenite porphyry which are shown to have anorthoclase (soda microcline) as the feldspar, and the author believes this to be a sufficient ground for the erection of a new rock group and proposes the names of hatherlite and pilandite for them respectively. Probably the majority of petrographers will hardly agree to this, since as commonly understood the syenite family is one composed essentially of alkaline feldspars in general and not one particular variety of them. As a matter of fact, the pure potash feldspar is of very rare occurrence as a rock-ingre-dient and the great majority of the so-called orthoclases contain the albite molecule to a greater or less extent. Moreover since the analyses of the feldspars of the rocks mentioned show that they contain a very considerable quantity of lime, it appears questionable whether they should not be classed as abnormal oligoclases rather than anorthoclase (soda microcline); they are clearly not typical examples of the latter.

Very full and painstaking investigations have been made in this work of the augitic constituents of the rocks mentioned which have been separated and analyzed, but it seems rather curious from modern standpoints that with so much chemical investigation of the constituents no mass analyses of the rocks except in one case have been made. This is a rock consisting of enstatite crystals including 4.5 per cent of anorthite plates. The analysis gave :

 $SiO_2$  $TiO_2$  $Al_2O_3$  $Fe_2O_3$ FeO Mg<sup>O</sup> CaO  $H_2O$ Sp. G.=3.3 2.08 29.29 1.68 1.12 = 100.0355.23 0.14 3.946.25

It is an enstatite pyroxenite from the Central Marico District.

10. On the Occurrence of Corundum.—Two recent papers on the occurrence of corundum in widely separated parts of the world deserve to be mentioned. One of these, by T. H. HOLLAND,\* discusses in detail the various corundum localities, including the gem varieties, ruby and sapphire, in India and the adjacent countries. The second paper, by W. G. MILLER,† describes the corundum and associated minerals of Eastern Ontario.

The most interesting point brought out in both papers is the fact that corundum occurs so often associated with igneous rocks; this fact has also been recently established in other regions. Mr. Holland accepts the fact that in certain cases it may have a secondary origin, as shown by Professor Judd for the ruby, but for the most part he regards it as an original constituent, though often due to the local excess of alumina. The Indian localities are divided into those in which the corundum occurs with basic rocks and these in which its associates are siliceous, that is, *acid*. In the former class pyroxene is the predominating constituent,

\* A Manual of the Geology of India: Economic Geology by the late Professor V. Ball. Second edition revised in parts. Part I, Corundum, by T. H. Holland; pp. 79, Calcutta, 1898.

+ Report of the Bureau of Mines, vol. vii, third part, pp. 207-265, Toronto, 1898.

together with some member of the spinel group. These occurrences are divided into three groups. In the first, the *ferruginous* group, the pyroxene is a highly ferriferous enstatite and the spinel either hercynite, or hercynite with magnetite; in this group ilmenite may largely replace the corundum. In the second, the *ferro-magnesian* group, ferrous oxide is largely replaced by magnesia, a less ferriferous enstatite and pleonaste, also sometimes chrysolite, being the type minerals. In the third, or *magnesian* group, iron compounds occur in very small quantity, the associated minerals being magnesian forms of chrysolite, also (secondary) tale, dolomite, magnesite.

In the second class, the corundum is associated with acid rocks. This is well illustrated by the sapphire of Kashmir, which occurs in granite; here the granite (pegmatite) forms veins in gneiss and carries with the sapphire, tournaline, euclase, cyanite, etc.; green tournaline, spodumene, cookeite and prehnite are also found. The gneiss is coarse and schistose, with white feldspar, black mica and also garnets.

The corundum of Ontario, as described by Mr. Miller, belongs chiefly to dikes of syenite and quartz pegmatite intersecting the Laurentian gneiss. It is found more abundantly in ordinary syenite than in nepheline syenite, but in the latter the crystals are better formed. It is also found in eastern Ontario in crystalline limestone, as in Burma, where it is regarded as of secondary origin. Mr. Miller's paper is accompanied by numerous interesting plates illustrating the actual occurrence of the mineral. Other mineralogical points are also brought out, as the occurrence of nickel-bearing magnetite, also of a mineral of the columbite type ( $G.=5\cdot40$ ), in Renfrew County.

11. Minerals in Rock Sections: The practical methods of identifying minerals in rock sections with the microscope. Especially arranged for students in technical and scientific schools. By LEA MCILVAINE LUQUER; pp. 117. New York, 1898 (D. Van Nostrand Company).—This subject has been already treated of by a number of authors, but there still remains place for the present volume. It gives in the opening chapters a concise summary of the optical principles, methods and instruments, and following a statement of the characters of minerals arranged with system and clearness. A chapter is also added on the methods of making sections and one on chemical tests. An optical scheme is added in the appendix.

12. New Mineral Names.—LAGORIOLITE. In connection with his important work in mineral synthesis and the crystallization of minerals from a molten magma, Morozewicz has obtained isometric crystals or crystalline grains of a mineral having the composition  $(Na_{a}Ca)_{s}Al_{a}(SiO_{4})_{s}$ , in which  $Na_{a}: Ca = 3:2$ . This corresponds to a sodium-grossularite, a type of garnet not yet noted in nature but which has peculiar interest as connecting the garnets with the minerals of the Sodalite Group. This compound is named after Prof. A. Lagorio.—Min. petr. Mitth., xviii, 147, 1898. THALENITE. A new yttrium silicate, having the composition  $H_2 Y_5 I_0 O_{10}$ . It occurs in tabular monoclinic crystals of a fleshred color. Hardness = 6.5; specific gravity = 4.229. Found in Österby in Dalecarlia, Sweden, and named by Benedicks after Prof. R. Thalén.—*G. För. Förk.*, xx, 308, 1898.

KTYPEITE. A name given by Lacroix to the calcium carbonate in the form of pisolites from Carlsbad and Hammam-Meskoutine in Algeria, which has formerly been referred to aragonite. The specific gravity varies from 2.58 to 2.70, or less than that of calcite. Optically the birefringence is 0.020. In parallel polarized light a distorted black cross is noted, while portions give a positive black cross in converging light. Heated to low redness, the pisolites decrepitate and are finally transformed into calcite; the name given refers to this fact. — Comptes Rendus, exxvi, 602, 1898.

### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The Benjamin Apthorp Gould Fund.—A circular has recently been issued by the Directors of the Gould Fund, Professors Lewis Boss, Seth C. Chandler and Asaph Hall, stating that a sufficient available income has now accrued to warrant beginning its distribution, and that they are prepared to receive and consider applications for appropriations. It will be remembered that the fund was established in November, 1897, when the sum of twenty thousand dollars was given to the National Academy of Sciences, as trustee, in memory of the father of the donor, Miss Alice Bache Gould, the income to be used to assist the prosecution of researches in astronomy.

In order to guide those desiring to secure appropriations from the fund, the directors make the following statement:

The objects of the institution are, first, to advance the science of Astronomy; secondly, to honor the memory of Dr. Gould by ensuring that his power to accomplish scientific work shall not end with his death. In recognition of the fact that during Dr. Gould's lifetime his patriotic feeling and ambition to promote the progress of his chosen science were closely associated, it is preferred that the fund should be used primarily for the benefit of investigators in his own country or of his own nationality. But it is further recognized both by the donor and the directors that sometimes the best possible service to American science is the maintenance of close communion between the scientific men of Europe and of America, and that, therefore, even while acting in the spirit of the above restriction, it may occasionally be best to apply the money to the aid of a foreign investigator working abroad. The wish was also expressed by the donor that in all cases work in the astronomy of precision should be given the preference over any work in astrophysics, both because of Dr. Gould's especial predilection and because of the present existence of generous endowments for astrophysics.

Finally, the Benjamin Apthorp Gould Fund is intended for the

advancement and not for the diffusion of scientific knowledge, and is to be used to defray the actual expenses of investigation, rather than for the personal support of the investigator during the time of his researches, without absolutely excluding the latter use under the most exceptional circumstances.

Application for appropriations from the income of this fund may be made informally by letter to any of the directors, stating the amount desired, the nature of the proposed investigation, and the manner in which the appropriation is to be expended. If favorably considered, a blank for formal application will be forwarded for signature, with the rules adopted by the directors for the administration of the fund, and to which the applicant will be expected to subscribe.

2. Annual Report of the Board of Regents of the Smithsonian Institution for the year ending June 30, 1896. Report of the U. S. National Museum; pp. xxiv, 1107. Washington, 1898.— The Report of the United States National Museum for the year ending June 30th, 1896, has recently been issued. It includes the report of the Assistant Secretary, the late Dr. G. Brown Goode, which gives, in addition to matters of current interest, an outline of the history of the Museum, showing how it has grown to its present dimensions. A series of Appendices relating to Museum matters follow.

Part II of the volume, covering nearly 750 pages, includes a paper entitled: An account of the United States National Museum by Frederick W. True (reprinted); also a series of ethnographical papers elaborately illustrated with many text figures and ful page plates. The first of these, by Thomas Wilson, discusses the origin of art as manifested in the works of pre-historic man; those not acquainted with the subject will be surprised to see what a variety of objects is here described and illustrated and how great interest attaches to them. The other articles are on Chess and Playing Cards by Stewart Culin; Biblical Antiquities by Cyrus Adler and I. M. Casanowicz; The Lamps of the Eskimo by Walter Hough.

3. The Second Washington Catalogue of Stars: together with the Annual Results upon which it is based. The whole derived from Observations made at the U. S. Naval Observatory with an 85 inch transit circle, during the years 1866 to 1891, and reduced to the epoch of 1875.0. Prepared under the direction of JOHN R. EASTMAN, Professor of Mathematics, U. S. N., Washington Observations for 1892, Appendix I, pp. lxiii, 287, Washington, 1898.—This large volume of star observations, as stated in the preface by the Director of the Observatory, Professor Harkness, has absorbed the labors of about two-thirds of the Observatory staff for more than thirty years, during the greater part of which time Professor Eastman was in immediate charge. His personal work included 17,334 observations of stars, out of nearly 73,000; and nearly 40,000 were made under his immediate direction. Professor Harkness adds that the credit and responsibility for the methods of discussing the observations, for the values of the systematic corrections applied in the formation of the final places, and for the arrangement of the volume rest with Professor Eastman.

4. Zoological Results based on material from New Britain, New Guinea, Loyalty Island and elsewhere, collected during the years 1895-1897; by ARTHUR WILLEY, Cambridge, England, Part II, pp. 121-206, plates xii to xxiii.—The first part of this important series of memoirs was noticed in the January number of this Journal (p. 79). The present part contains the following seven papers: 7, Report on the specimens of the genus Millepora, by S. J. Hickson, pl. xii-xvi; 8, On the Echinoderms (other than the Holothurians) by F. Jeffrey Bell, pl. xvii; 9, Holothurians, by F. P. Bedford, pl. xviii; 10, On the Sipunculoidea, by A. E. Shipley, pl. xviii; 11, On the Solitary Corals, and 12, On the postembryonic development of Cycloseris, by J. Stanley Gardiner, pl. xix, xx; 13, On a collection of Earthworms, by F. E. Beddard, pl. xxi; 14, On Gorgonacea, by Isa L. Hiles, pl. xxii, xxiii. Part III is stated to be now in press.

5. A Select Bibliography of Chemistry, 1492-1897; by HENRY CARRINGTON BOLTON. First Supplement; pp. ix, 489. Washington, 1899. (Smithsonian Miscellaneous Contributions, 1170.).-Workers in science owe much to the careful and painstaking labors of those who prepare the bibliographies in the different departments. One of the most complete of these is the Bibliography of Chemistry, 1492-1892, by Professor Bolton, which was issued in 1893. A First Supplement to this work has now been issued, bringing the literature of the subject down to the close of 1897. This is a closely printed volume of nearly five hundred pages, which fact alone gives evidence of the large amount of material brought together. The total number of titles is 5554 in twenty-five different languages; these titles are classified under the following seven heads: Bibliography; Dictionaries and Tables; History of Chemistry; Biography; Chemistry, Pure and Applied; Periodicals. 6. Biological Laboratory.-The Biological Laboratory of the

6. Biological Laboratory.—The Biological Laboratory of the Brooklyn Institute of Arts and Sciences will be located for its tenth season at Cold Spring Harbor, Long Island, during the months of July and August, 1899. The director of the laboratory is Charles B. Davenport, Ph.D. of Harvard University. A circular giving the names of instructors, courses of study offered, equipment and other details has recently been issued, and copies may be obtained from Prof. F. W. Hooper, 502 Fulton st., Brooklyn.

# CANARY-YELLOW URACONITE



A new and small find of this rare and beautiful Uranium mineral. recently made in Colorado, has all come to us. The specimens are even more attractive than those in the little lot secured a year ago, which received so warm a welcome from collectors, and include several large size specimens at \$1.00 to \$6.00, and an excellent assortment of smaller cabinet sizes at 15c. to \$1.00.

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# AMERICAN JOURNAL OF SCIENCE

# [FOURTH SERIES.]

ART. XXXIV.—On some Experiments with Endothermic Gases; by W. G. MIXTER.

[Contributions from the Sheffield Laboratory of Yale University.]

THESE experiments were made in U-tubes of 30 to 50<sup>cm</sup> in length and for high pressures the form shown in fig. 1 was



employed. The part above the electrodes a a was narrowed for convenience in opening the tube and measuring small residual quantities of gases. The other end was connected by means of a small copper tube with a hydraulic pump. At b

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#### 324Mixter-Experiments with Endothermic Gases.

was a thick wrapping of cotton wicking to protect the rubber stopper from the wire used to hold it in place. Such a connection answered for a pressure of 20 atmospheres by the pump and withstood explosions that burst the other limb of the Utube. For filling the apparatus a little mercury was poured in to form a trap at the bend and the air was displaced by passing in a liter or more of gas through a small rubber tube reaching to the closed end; then more mercury was added, the stopper adjusted, the apparatus placed in a tall glass jar to prevent danger from flying glass and to catch the mercury in case the tube broke. The desired pressure was obtained by forcing in water with a pump. For pressures of three atmospheres or less a reservoir of mercury connected by means of a rubber tube was convenient, the heighth of the mercury in the reservoir above its surface in the U-tube being the measure of the pressure. For heating gases by a glowing wire the end with the electrodes in fig. 1 was modified as indicated in fig. 2. To the heavy copper wires passing through the rubber stopper was soldered a platinum wire which was made to glow or even melt by a battery current.

### Acetylene.



Berthellot and Vieille\* have investigated the explosion of acetylene, and hence it is only necessary to state that my results, obtained before their paper was published, accord with theirs and that they are briefly given in order to show that the other endothermic gases tested do not explode in the same apparatus and under the same conditions. At a pressure of two atmospheres when an electric spark was passed or a platinum wire was made to glow in the gas it sometimes did not explode, while at a pressure of three or more atmospheres explosions always occurred. If, however, the sparks are small acetylene does not explode even at high pressures. A number of tests were made in a tube shown in part in fig. 3, containing acetylene under various pressures up to 20 atmospheres; when the inner and outer wires were connected with an induction coil in action, sparks visible in strong daylight passed between the glass and the inner wire. This form of discharge did not cause explosion. When it continued for some

time a reddish deposit appeared. This was insoluble in ordinary solvents, and exploded when heated, leaving a black residue. It was not further investigated. The presence

\* Compt. Rend., cxxiii, 523.
#### Mixter—Experiments with Endothermic Gases. 325

of an indifferent gas checks the explosion of acetylene, as the following show: A dry mixture of 1 volume of acetylene and 2 volumes of hydrogen at a pressure of 5 atmospheres was not exploded by sparking; carbon separated slowly but there was no cloud of soot. The result was the same with equal volumes of the two gases at 6 atmospheres, while with a mixture of 2 of acetylene and 1 volume of hydrogen at 5 atmospheres, the explosion promptly followed the electric discharge. The spark used was  $2^{cm}$  in air and was passed between electrodes  $3^{mm}$ apart in the gas.



The following experiment illustrates beautifully and simply the endothermic character of acetylene and also shows that a dull red heat is sufficient to decompose it. A slow current of the gas is passed through the tube a, fig. 4, into the larger tube, which is heated as shown by a Bunsen burner. When the part of the outer tube about the end of a is heated to a faint glow there is a slight puff and then the gas issuing from the end of a glows or rather the carbon, separating beyond the end of the little tube, glows. It is a jet of gas filled with a cloud of lampblack glowing with the heat resulting from the flow of the gas must be carefully regulated. If too fast, the gas does not attain the temperature of decomposition, and if too slow it does not glow.

#### Cyanogen.

Experiment 1.—The U-tube, fig. 1, was charged with cyanogen made from dry mercuric cyanide. The gas was nearly free from air or other permanent gases, as it was found that  $100^{\circ\circ}$  left only a small volume of gas when liquefied by pressure. When induction sparks were passed through the vapor of cyanogen at a pressure of about five atmospheres, at which a portion of the compound was liquid, carbon separated at once and connected the electrodes. There was no explosion and no decomposition except in the path of the spark. A primary current from two large storage cells was next passed, the carbon filament connecting the platinum wires in the tube

# 326 Mixter—Experiments with Endothermic Gases.

serving as a conductor. The result was a brilliant violet light and the separation of a little more carbon. The primary current had, however, broken the filament so that on connecting again with a coil in action sparks passed, but soon ceased. The primary current then gave the same result as before. The amount of cyanogen decomposed was small, for of the  $100^{\circ\circ}$ taken only  $1^{\circ\circ}$  was not absorbed by potassium hydroxide after the experiment.

Experiment 2.—Cyanogen was condensed in the apparatus fig. 2 until a portion liquefied, and the wire was heated white hot by a current from a battery. A slight fog appeared but there was no separation of carbon throughout the gas, and there was no explosion. The result was the same at lower pressures. Finally the platinum wire was melted in the gas at the pressure of liquefaction, but there was no explosion nor any considerable decomposition. A thin coating of carbon had formed on the wire.

#### Nitrous Oxide.

*Experiment 1.*—The apparatus, fig. 1, was filled with  $72^{\text{ec}}$  of pure dry nitrous oxide, and the gas was condensed to  $6^{\text{ec}}$  and sparked. There was no explosion. Faint red fumes appeared. On lowering the pressure after the sparking to that of the atmosphere, the gas showed increased volume but not 50 per cent, as would have been the case had the dissociation been complete.

*Experiment* 2.—100<sup>cc</sup> of gas condensed to  $5^{cc}$  and finally to  $3^{cc}$  were sparked for some time. There was no explosion and the volume at the close of the experiment was less than  $150^{cc}$ .

Experiment 3.— $70^{\circ\circ}$  of nitrous oxide were condensed to  $5^{\circ\circ}$  and sparked. The result was the same as in the preceding experiments.

*Experiment*  $4.-100^{\circ\circ}$  of nitrous oxide condensed to  $10^{\circ\circ}$  were sparked. There was no explosion.

In the above tests the platinum electrodes were  $4^{mm}$  apart and the spark used was fairly strong and had a length in air of  $3^{cm}$ .

#### Nitric Oxide.

*Experiment* 1.—Dry nitric oxide was sparked at pressures varying from 12 to 20 atmospheres. There was no explosion, but the gas became reddish.

*Experiment* 2.—100<sup>cc</sup> of dry nitric oxide were condensed to 10<sup>cc</sup>. The spark and electrodes were as described under nitrous oxide. The first spark through the gas produced a small flame between the electrodes. The sparking was continued only a

few seconds. The gas remaining was nearly all absorbed by a solution of ferrous sulphate, showing that only a small portion of the nitric oxide had been decomposed.

*Experiment* 3.— $50^{\circ\circ}$  of gas were condensed to  $6^{\circ\circ}$  and sparked a short time. After treatment with ferrous sulphate only  $0.5^{\circ\circ}$  remained.

The deportment of nitrous and nitric oxide in the above tests is much the same as in the well known experiments of sparking these gases at ordinary pressure.

The results of the experiments described in this article will be discussed in the next paper.

# ART. XXXV.—On a Hypothesis to explain the partial nonexplosive Combination of Explosive Gases and Gaseous Mixtures; by W. G. MIXTER.

[Contributions from the Sheffield Laboratory of Yale University.]

MUCH has been done in investigations of the conditions under which gases combine gradually or with explosive violence. The velocity of explosive waves has been determined, and the influences of pressure, and of excess of one gas or dilution with an indifferent one, have been studied. Dixon\* states, "The explosive wave is propagated not only by burnt molecules, but also by those of the heated but yet unburnt molecules." But so far as the writer is aware, no hypothesis has been advanced to account for the fact that explosive mixtures will not explode at low pressures, and that weak electric sparks may not cause explosions, where strong sparks do. Victor Meyer, with the aid of his pupils, has made a large number of experiments with explosive mixtures at different temperatures and pressures, but he has offered no explanation of the phenomenon of slow combination in such mixtures. As the union of hydrogen and oxygen has been more thoroughly studied than that of other gases, the deportment of detonating gas, by which is understood equivalent amounts of hydrogen and oxygen, under various conditions, affords the best basis for discussion. The behavior of certain other gases, and the observations of different experimenters, will also be considered.

Dixon<sup>+</sup> found that detonating gas at a pressure of 70<sup>mm</sup> does not explode when an electric spark is passed through it, and

\* Chem. News, lxvii, 39.

† Trans. Roy. Soc., 1884, 634.

L. Meyer and Seubert<sup>\*</sup> observed at the same pressure that three-fourths of the gas combined. The writer noticed+ that weak sparks did not cause an explosion of the gas. This is not peculiar to detonating gas, as Dixon<sup>‡</sup> states that "The explosion of cyanogen and oxygen depends solely on the nature of the spark. A strong spark causes the mixture to explode violently, whether wet or dry. A weak spark may be passed through the mixture, wet or dry, without apparent effect."

Emich<sup>§</sup> has recently studied the inflammability of thin layers of explosive mixtures of gases, and has found that the length of the spark required for ignition bears an inverse relation to the density, and that the addition of oxygen to detonating gas till it is to the hydrogen as 1:1 increased the sensitiveness of the mixture to sparks; an analogous fact obtains for an explosive mixture of hydrogen and chlorine. On the contrary, equivalent mixtures of carbonic oxide and oxygen are more sensitive than those containing an excess of either.

The glow discharge of electricity produces gradual combination of explosive mixtures. Meyer and Raum experimented with detonating gas in sealed bulbs, and observed no perceptible combination after exposure for 218 days, to a temperature of 100°, while after 65 days, at 300°, they found in three tests that 9.5, 0.4, and 1.3 per cent of the gas had united. They obtained at 350° and 50 hours, 1.6 per cent, and after 120 hours, 1.9, 16.4, 0.5, 0.7 per cent. Krause and Meyer\*\* found that 28 to 100 per cent of detonating gas combined when heated to 518° for 2 hours, in sealed bulbs. On the other hand, Askenasy and Meyer++ observed that but little water was formed where the gas passed slowly through a vessel at 606°. Freyer and Meyer<sup>‡‡</sup> determined the temperatures at which mixtures of gases exploded when slowly passing through a hot vessel, and also when quickly heated in sealed bulbs. Explosions occurred at the higher temperatures given in the following table, but not at the lower:

		current.	bulbs.
Hydrogen		650-730°	518-606°
Methane	with	$650 - 730^{\circ}$	$606 - 650^{\circ}$
Ethane	oxygen	606-650°	$518 - 606^{\circ}$
Ethylane	required	$606 - 650^{\circ}$	$518 - 606^{\circ}$
Carbonic oxide	for complete	$650 - 730^{\circ}$	650-730°
Hydrogen sulphide	combustion	315-320°	$250-270^{\circ}$
Hydrogen and Chlorine		430-440°	$240 - 270^{\circ}$

\* Jour. Chem. Soc., xlv, 587. t J Chem. Soc., xlix, 384. This Journal, iv, 51, 1897.

\*\* Liebig's Ann., cclxiv. 85

+ This Journal, iv. 51.

§ Monatsheft f. Chem., xviii, 6, xix, 299.

Ber. d. deutsch. Gesell., xxviii, 2804.

With fuce

boloor

++ Liebig's Ann., cclxix, 49.

11 Zeitschr. für phys. Chem., xi, 28.

They also found that detonating gas suddenly heated in unsealed bulbs exploded at the same temperature as in sealed.

Before discussing chemical changes let us recall the condition of matter in gases—the molecules are moving very rapidly, some faster, some slower, an individual molecule moving in a straight line for a very short distance, until it strikes another. These collisions of one molecule with others are very frequent. The atoms composing a molecule are also moving in respect to each other, this motion constituting a portion of the internal energy of the molecules, which is continually diminishing through radiation. When the gas is heated the mean velocity of the molecules is increased, and at the same time the atomic motion and internal energy are also increased. At a sufficiently high temperature some of the collisions are so violent as to disrupt the molecules and their atoms part company.

When a mixture of gases is heated, chemical combination results from the encounters of different kinds of molecules having motion of translation, or of the atoms, or of both. At any given temperature the mean velocity of molecules may be calculated, but we have no data for determining at what greater velocity the molecular collisions are followed by chemical union. Polyatomic molecules are dissociated by heat, but since there is no measurable dissociation of hydrogen or oxygen at 1600° it does not appear that dissociation by heat plays much part in the change. Whatever the chemical changes caused by heat in gases, whether combination or dissociation, the condition necessary for these changes results from molecular impacts. If, for example, detonating gas be heated, a part of the molecules acquire a velocity and internal energy adequate for combination. Some of these encounter each other and combine to form water, the free atoms of oxygen uniting with each other or with hydrogen. The nascent water molecules have in general a high velocity, and collide with those of oxygen and hydrogen; but it is not probable that a single impact of a new water molecule with one of hydrogen or oxygen imparts to the latter energy adequate for combination. If it were so, the change would proceed with accelerating speed at a temperature of 300° to 500°. This view, that a nascent water molecule does not necessarily cause hydrogen and oxygen to unite, accords with that expressed by the writer,\* that the heat of combination caused by the glow discharge of electricity does not produce further combination.

Why is it that chemical union proceeds slowly at 500°, and why does not the energy resulting from combination cause further combination, and thus raise the temperature of the sys-

\* This Journal, vi, 218, 1898.

## 330 Mixter—Partial non-explosive Combination of

tem to the point of explosion? Let us suppose the mixed gases be heated from 500° to 501°. This increase in temperature will not cause them to explode. Assume further, that the heat of combustion during one minute is sufficient to raise the temperature of the gases 1°, provided no heat is lost by radiation. Experiments have shown that this rise in temperature will not cause explosion. But the gases heated by their own slow combustion continually lose heat by radiation, and hence are only slightly hotter than the surrounding medium. Were it possible to prevent loss of heat, the temperature would rise and the change proceed with accelerating speed.

The observations of Freyer and Meyer (loc. cit.), that explosive mixtures gradually heated have a higher ignition point than when suddenly heated, are difficult to explain, and further experiments may be useful. Their results also indicate that pressure is without influence, while A. Mitscherlich\* found that at pressures less than one atmosphere the ignition point falls with the pressure. As pressure in so many cases influences explosion, it is remarkable in Freyer and Meyer's experiments that detonating gas in an open vessel, when quickly heated, exploded at the same temperature as it did under a pressure of two atmospheres or more. Mitscherlich's results also are the opposite of what we might expect.

Let us first consider the phenomenon of explosion of detonating gas at a low pressure when the combination is not complete. An electric spark or hot wire ignites the gas, the water molecules about the source of heat collide with the neighboring ones of hydrogen and oxygen, molecules of these elements being shaken up by many impacts and acquiring energy adequate for combination, and thus uniting and adding energy to the system. In this way the change propagates itself. A part of the molecules of hydrogen and oxygen have not combined. Why? When a denser gas is ignited, the combination is complete, and as the temperature of burning hydrogen is sufficient to dissociate water, we must assume that some of the water molecules are broken up, and as the temperature falls they reform, all of the hydrogen and oxygen uniting before the temperature is too low for combination. In the case of the rarer gas, the impacts to which a molecule of hydrogen or oxygen is subject from the nascent water molecules are less frequent than in the denser gas, and hence it is not as likely to acquire the energy needed for chemical union. Moreover, molecules possessing velocities adequate for combination encounter each other less frequently in the rare gas; hence the chemical change will proceed more slowly, and there will be more time for the system to lose heat by radiation. A

\* Ber. d. deutsch. Chem. Gesell., xxvi, 399.

molecule with internal energy adequate for combination loses this energy if its free path is relatively long; that is, given sufficient time though very brief, the molecule assumes a condition unfavorable to chemical union.

Let us now see if other phenomena are explained by this hypothesis, considering first the case of an electric spark in detonating gas at a pressure too low for explosion. Here we have an enormous number of molecules combining in the luminous path of the spark. These radiate energy, part being electrical in its origin, i. e., a portion which was derived from the external work done upon the gas, and part resulting from chemical union. These encounter neighboring molecules of hydrogen and oxygen, imparting to some of them energy adequate for combination. Of these last a part combine, and we have now to consider a portion of gas consisting of water molecules, as well as those of hydrogen and oxygen. Some of the last named possess energy adequate for chemical union, but their encounters are too infrequent to restore by the heat of combination the energy radiated, hence the change proceeds with diminishing speed and finally ceases to propagate itself.

Feeble sparks do not explode detonating gas at a pressure of half an atmosphere or even more, but they cause slow combination. In this case it is not necessary to consider the possibility of the hydrogen carrying the electricity, since water molecules are formed, and we need only take into account a system made up of a relatively small number of nascent molecules of water, molecules of hydrogen and oxygen having energy adequate for combination, together with a relatively large number of molecules of these gases not having such energy. Under these conditions the impacts resulting in chemical union are too infrequent to maintain by the heat of their combustion the energy lost by radiation, and consequently the change does not propagate itself and cause an explosion.

Carbonic oxide and oxygen combine slowly at pressures less than an atmosphere when subjected to feeble sparks. Here too the impacts of molecules with a velocity adequate for chemical union are infrequent, as is evident from the fact that the change does not propagate itself.

In the case of cyanogen and oxygen either the feeble spark causes no chemical union, which is improbable, or as in the previous instances the change does not proceed throughout the gas because of the infrequency of impacts of high velocity molecules.

The study of the phenomena of explosives involves the thermal effect, but for the present purpose the heat evolved by the explosion or decomposition of equal volumes will suffice. Two grams and 2 volumes of hydrogen burn with 1 volume of oxygen, with a thermal result of 58,700 calories, the product gaseous; and 2 volumes of the mixture, therefore, give 39,134 c. Likewise, 2 volumes of carbonic oxide and oxygen give 45,312 c.; 1 volume of hydrogen and 1 of chlorine give 22,000 c.; and 24 grams of solid carbon and 2 of hydrogen unite with an absorption of 48,170 c. to form 2 volumes of acetylene, which evolves this amount of heat when resolved into its elements. In the same way, we have for cyanogen 65,700 c., for nitrous oxide 17,470 c., and for nitric oxide 21,575 c. set free when these compounds are decomposed into their elements. The following table gives the resultant heat of the combination of equal volumes of three mixtures, and of the decomposition of four endothermic gases:

I	Resultant heat.	Nature of product.
Hydrogen and oxygen	. 39134	Gaseous
Hydrogen and chlorine	. 22000	"
Carbonic oxide and oxygen.	45312	66
Acetylene	- 48170	12 / 13 solid
Cyanogen	- 65700	12 / 21 "
Nitrous oxide	. 17470	Gaseous
Nitric oxide	_ 21575	"

The molecular heats at constant volume of  $H_2$ ,  $O_2$ ,  $N_2$ , CO, NO, and HCl are 4.2 to 5, and of  $N_2O$ ,  $H_2O$ , and  $CO_2$ , about one-half larger. Those of  $C_2H_2$  and  $C_2N_2$  do not appear to have been determined, but they are probably not greater than 10. Evidently the molecular heats have little influence in determining the temperature at which explosion occurs, and the resultant heat does not account for the fact that the ignition temperature of chlorine and hydrogen is much lower than that of hydrogen and oxygen, or of carbonic oxide and oxygen.

Acetylene requires a pressure 20 times greater than detonating gas for explosion, while the heat of decomposition of the former exceeds that of chemical union of the latter. At temperatures not high enough to cause acetylene to separate completely into its elements or cause detonating gas to explode, the two gases exhibit similar deportment in this respect, namely, that the change is one of slow combination. Acetylene polymerizes to form  $C_sH_s$ ,  $C_sH_s$ , and other condensation products, and detonating gas forms water. But acetylene, when sparked under sufficient pressure, decomposes completely into carbon and hydrogen. The impacts of acetylene molecules with a certain velocity causes them to combine with each other, but when they have a higher velocity complete decomposition results. The change started by a spark in dense acety-

lene propagates itself throughout the gas. About the path of the spark there are sufficiently numerous encounters of molecules with a velocity adequate to cause decomposition, and the heat resulting is not lost by radiation before other molecules of acetylene are decomposed. Thus the change continues until only solid carbon and stable molecules of hydrogen remain. A proposed method for the commercial production of lampblack depends upon this fact. When, however, a spark passes through the gas at common pressure, the change occurs only in the path of the spark. Here the impacts of molecules with a velocity adequate to cause decomposition are more infrequent than in the denser gas-too infrequent, as the result shows, to propagate the change. The heat about the path of the spark is dissipated by radiation before it decomposes neighboring molecules. The infrequency of impacts allows sufficient time for radiation, and for the molecules to assume a stable condition. It is also probable that some more stable molecules, such as C.H., are formed. If acetylene issuing from a tube is lighted, the decomposition does not extend into the tube for the same reason that it does not extend through the gas when sparked at ordinary pressure.

The deportment of acetylene under high pressure, when subjected to small sparks (p. 324) is similar to that of detonating gas.\* Condensation products are formed in one case and water in the other. The minute spark imparts to the molecules of acetylene energy adequate to effect combination, and as the spark is visible we assume that the portion of the gas which is glowing has a temperature at which acetylene decomposes when larger quantities are heated. Thus the infrequency cf impacts of molecules of high velocity is the real reason why feeble sparks do not start an explosion in dense acetylene.

The non-explosion of cyanogen (p. 325) under high pressure when sparked, although it is more endothermic than acetylene, is doubtless connected with the fact that it requires a higher temperature for its decomposition than the latter; or it may be that the union of CN with CN is exothermic, while the radical itself is endothermic. Nitrous oxide and nitric oxide are stable at high temperatures and these also do not decompose with explosive violence when sparked under pressure. It is probable that all three of these endothermic gases would explode if sparked under pressure and at a temperature approaching that at which they dissociate.

\* This Journal, iv, 51.

# Recapitulation.

Detonating gas, a mixture of carbonic oxide and oxygen, one of cyanogen and oxygen, and other explosive mixtures of gases do not explode below certain pressures when sparked: and the decomposition of acetylene does not propagate itself at pressures less than two atmospheres. In the path of the spark chemical changes occur which do not extend throughout the gases, and the same is true of a weak spark in the gases mentioned when under a pressure at which a strong spark explodes them. It appears for reasons already stated that explosions do not occur in the instances given only because of the infrequency of impacts of molecules having a velocity or internal energy adequate for chemical union. In the rare gas the impacts are less frequent than in a dense gas, the mean free path is longer, and there is more time for a molecule with energy adequate for combination to lose this energy by radiation and to attain a condition unfavorable to chemical union. Some of the molecules combine, but the heat of their union is not sufficient to restore the energy lost by radiation and the change is therefore not self-propagating. The same explanation holds good for the phenomena of feeble sparks in a dense explosive gas where in the path of a spark there are relatively few molecules with energy adequate for combination, and these collide with each other less frequently than with the molecules not having such energy. In a dense gas a given quantity and a degree of heat, that is, sufficient frequency of molecular impacts, is requisite to secure spontaneous extension of the change.

Williams-Occurrence of Paleotrochis in Mexico. 335

# ART. XXXVI.—On the Occurrence of Paleotrochis in Volcanic Rocks in Mexico; by HENRY S. WILLIAMS.

Introductory Note.—This article was written, Nov. 22, 1897, at the time of the study of the specimens sent by Dr. Dugès, but for various reasons was not then published. A discussion in the Geological Society last December led the writer to refer to these specimens as proof of the non-organic nature of Paleotrochis. Later the Mexican specimens, together with the manuscript copy of this paper, were sent to Mr. Walcott and then to Mr. Diller in confirmation of the inorganic origin, and association with igneous rocks, of Paleotrochis. It is thought best to publish these facts for what they are worth, in connection with Mr. Diller's thorough study of the subject as presented in the following paper.

SOME specimens sent to Yale College for identification, by Dr. Alfred Dugès of Guanajuato, Mexico, throw some light upon the nature of the peculiar forms described by Emmons under the name of Paleotrochis. The specimens come from what appears to be an old eroded volcanic cone made up of "Porphyre altéré," "Peckstine rouge" and volcanic tuffs, situated northeast of Guanajuato in the Santa Rosa Mountain range. Among the specimens are several fragments of much altered fragmental as well as massive volcanic rocks. One specimen is filled with amygdules.

The majority of the specimens are composed of milky quartz of the shape called Paleotrochis by Emmons, with variations in form which are particularly suggestive. These suggestive variations are the imperfect form, one-sided, or as if made up of several of the conical halves of typical paleotrochis joined together at their bases, some of the cones being very broad and nearly flat, but each having the appearance of accretion from the small end which in the lower cones is near the center. When thus nearly flat the lines of concentric accretion are evident, while the cones with less angle of slope show the radiating lines more conspicuously. The suggestion furnished by their study is that they were formed in a manner similar to that of the formation of ice columns under a loose soil, which at about freezing temperature sometimes grow to several inches in length. The lengthening of the column of ice, in the latter case, appears to be due to additions of ice forming as soon as the cool atmosphere is reached, while the temperature of the soil is still enough below freezing to permit the water to be drawn up by capillary flow to the surface as the freezing removes it from the surface immediately below.

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In the case of the Paleotrochis the application of the suggestion would be in this wise : If a' porous rock, had arising through it from below, superheated waters carrying solution of silica, a point might be reached when suddenly the looseness of the rock would permit of rapid radiation upwards of heat, while below the temperature of the heat would be high and remain nearly constant for a long period. Such conditions might occur along the plane of a considerable exit of the rising waters, the rocks below being saturated with the heated waters and above the rock being more or less open by the absence of water. I conceive that, at the junction, a condition might occur in which silica would begin to deposit on the interior of a cavity, but the supply of silica, or of silicated waters, would Thus be furnished only as it was abstracted by solidification. at the points where solidification began the cavity would be increased by the crystallization, and into this cavity more silicated waters would arise; thus the accretion-surface would increase with the lengthening of the cone by the separation of the apices of the cones; consolidation taking place at the point of meeting of the solidified silica with the water, and the water reaching that point slowly.

If some such explanation be the fact, the association of these peculiar forms with gold is explained. Also that such conditions should occur in volcanic regions and particularly in the midst of volcanic tuffs, as in the Mexican case, is as would be expected.

Nov. 22, 1897.

# ART. XXXVII.—Origin of Paleotrochis; by J. S. DILLER.

PROF. EBENEZER EMMONS,\* while State Geologist of North Carolina, discovered among the so-called Taconic rocks of Montgomery County, in that State, a number of more or less regularly striated bi-conical forms to which he gave the names Paleotrochis major and minor, and regarded them as siliceous corals as well as the oldest representatives of animal life upon the globe. According to Émmons Paleotrochis varies in size up to two inches in diameter, and occur with many almond shaped concretions, often within concretions, in a series of beds over 1,000 feet in thickness interstratified with beds of granular quartz, conglomerate and quartzite. Both species of Paleotrochis have the form of "a flattish double cone applied base to base" with the surfaces grooved somewhat irregularly from near the apex to the basal edge. The smaller form, P. minor, has the "apex of the inferior side excavated or provided with a small roundish cavity" and the other apex "supplied with a small rounded knob, from the base of which the radiated grooves begin." The larger form, P. major, "differs from the foregoing (P. minor) in the absence of the roundish apical depression of the lower side and the knob of the opposite side."

Prof. Emmons regarded Paleotrochis not only as originally siliceous but also gemmiferous, thus accounting for knobs as well as irregular adhering groups, and it is important to note that he reports "these fossils also occur in a variety of quartz or quartzite which I have described as a buhrstone, and which is often porphyrized."

Prof. James Hall, + after an examination of many specimens, regarded the Paleotrochis of Emmons as nothing but concretions in quartz rock. Prof. O. C. Marsh; examined the forms microscopically and found them composed of fine-grained quartz, but no trace of organic structure could be detected. While maintaining its inorganic nature he regarded it as difficult to explain, and considered it as having some analogy with cone-in-cone, which he thinks is probably due to the action of pressure on concretionary structure when forming.

The most extensive paper on this perplexing form is that of Mr. C. H. White, § who strongly advocates the organic nature

Journ. of the Elisha Mitchell Scientific Soc, Chapel Hill, N. C., Part 2d, July to December, 1894, pages 50-66.

<sup>\*</sup> Geological Report of the Midland Counties of North Carolina, 1856, page 62, also this Journal, II, vol. xxii, page 390, and vol. xxiv, page 151. † This Journal, II, vol. xxiii, page 278.

t This Journal, II, vol. xlv, page 218.

of Paleotrochis. The specimens he examined were those obtained by Prof. Emmons, as well as a number collected by Prof. J. A. Holmes, the present State Geologist of North Carolina. Mr. White describes in detail not only the peculiarities of the weathered surface of the rock but also the features exhibited upon a fresh fracture, and called attention for the first time to the radial fibrous mineral which he regarded as impure chalcedony. According to Mr. White, the fossil forms are enveloped in chalcedony and the small concretions are made of the same material.

In 1887, Prof. J. A. Holmes\* visited the Sam Christian Gold Mine of Montgomery County, N. C., and studied the Paleotrochis-bearing rock in the field. Although he had not then seen any of the acid volcanic rocks from New England, described by Dr. M. E. Wadsworth, or from the South Mountain region of Maryland and Pennsylvania, subsequently described by Dr. G. H. Williams and Miss Florence Bascom, he was of the opinion that the rocks in the neighborhood of the Sam Christian Gold Mine were of eruptive origin. Later observations have convinced him of the correctness of this The same opinion is entertained by Messrs. H. B. C. view. Nitze and George B. Hanna, who consider the Paleotrochisbearing rocks at the Sam Christian and Moratock Mines as ancient acid volcanics, and state that "it appears highly probable that at least some of these siliceous pebbly concretions are spherulites." Unfortunately in the preparation of their report time did not permit the authors to study thin sections.

The specimens which, at the request of Mr. C. D. Walcott, the Director of the U. S. Geological Survey, the present writer has had an opportunity to study, consist of a small collection‡ from Mexico sent by Prof. H. S. Williams, besides three fragments about nine inches in diameter sent by Prof. J. A. Holmes, who collected them in 1887 at the Sam Christian Gold Mine, North Carolina, and from the same place several dozen of the original specimens of Paleotrochis major and minor collected by Prof. Emmons. Specimens of the rock and isolated fossils, excepting those from Mexico, have been cut and polished and thin sections prepared for microscopical study.

The rock from North Carolina which contains Paleotrochis is full of nodules of various shapes and sizes, ranging from that of a pin's head to nearly two inches in diameter. These are the supposed concretions and fossils. Upon a fresh fracture the rock appears to be composed chiefly of quartz, but when

<sup>‡</sup> See Prof. William's article, this volume, page 335.

<sup>\*</sup> Letter to the author Feb. 6, 1899.

<sup>+</sup> North Carolina Geological Survey, Bul. No. 3, pages 37 and 39.

weathered most of the nodules become white as if kaolinized, while the other nodules and the matrix remain quartzose in appearance. The nodules form at least two-thirds of the mass of the rock and are arranged with their longer diameters parallel, rendering the rock rather easily split in one direction.

With a lens, it may be seen that the small kaolinized nodules exposed in section upon the surface of a hand specimen have a radial fibrous structure. The same structure may be seen in some of the larger ones, and in addition to this feature some of the nodules possess a more or less distinct concentric shelllike structure. These structures are usually best displayed upon or close to a weathered surface. Portions of the nodules or spaces between them are in a few cases cellular, and the walls of the openings are rarely lined with minute crystals. The supposed fossil forms usually appear conical or discoidal upon a weathered surface. They often show a small cup in the apex and are surrounded by a narrow depression from which the radial fibrous envelope pointed out by Mr. White has been removed by weathering.

A careful comparative study of the nodules in the hand specimens tends to convince one that however different in form and size the supposed fossils and concretions may appear, all belong to one series and have essentially the same origin.

A microscopical study of thin sections of the rock reveals the fact that the nodules are spherulites, a common feature of acid igneous rocks. They are composed in most cases chiefly of fibrous feldspar with quartz or tridymite. As seen in the thin section of the Paleotrochis-bearing rock, the fibers are grouped radially with more or less irregularity in tufts, sheaves, sectors, hemispheres or spheres. When they form a complete sphere, which is rarely the case, they are most coarsely fibrous or granophytic at the center and usually show between cross nicols an indefinite black cross. Occasionally also the concentric structure is well marked. The rays are too minute to permit of an accurate determination of their mineral composition by optical methods, but microchemical tests with hydrofluosilicic acid yield the small cubic crystals, characteristic of potassium fluosilicate as well as the hexagonal prisms of sodium fluosilicate. Judging from the greater abundance of prisms than cubes the fibrous feldspar is richer in sodium than potassium. That feldspar, instead of chalcedony, is the most prominent constituent of the spherulites, is fully borne out also by its kaolinizing under the influence of the weather.

The spherulites are embedded in a matrix composed chiefly of granular quartz. The grains are occasionally so large that the uniaxial positive character can be readily determined. Untwinned feldspar in small grains may be present in con-

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siderable amount and yet be easily overlooked. The quartzose character of the weathered matrix, however, shows that at least where most coarsely granular there cannot be much if any feldspar present in it. In places the matrix contains numerous minute parallel scales of what appears to be sericite. Associated with the most coarsely crystalline areas are a few scales of brown biotite and occasionally considerable green biotite, which in places is so abundant as to make quite prominent dark green spots. Both matrix and spherulites are traversed in a few cases by small veins of granular quartz, showing that there is a considerable amount of secondary quartz present. Both spherulites and matrix are rendered slightly microporphyritic by containing occasional crystals of plagioclase, feldspar and quartz. The plagioclase, which, on account of its small angle of symmetric extinction, must be an acid one, in some cases forms the center from which the spherulitic fibres radiate.

An isolated specimen of Paleotrochis was cut through the apices and found to be composed of granular quartz. The quartz was fine-grained upon the outside where the grains were set with their longest axes perpendicular to the adjoining surface. The middle portion contained an irregular iron-stained cavity possibly due to the disappearance of some iron-bearing mineral. Several of the half embedded forms of Paleotrochis were cut in a hand specimen to discover its relations to the enclosing rock, and in each case it formed the interior portion of a spherulite. Most of them contained a dark green patch. The exposed conical surface of one was well striated and there was an irregular depression in the apex. The form was composed chiefly of granular quartz with a yellowish brown to dark green, strongly pleochroic biotite. Near the center is a small spherulite which is not only bordered by finer-grained quartz but is cut by a small vein of it, showing that the deposition of the quartz is subsequent to the development of the spherulite. The embedded portion of Paleotrochis is bordered by spherulitic fibers which run approximately parallel to the slope of the conical surface, and it is evident that the casts of these fibers produce the irregular striæ or grooves upon the surface of the supposed fossil. The embedded portion terminated with an irregularly-pointed apex below. The whole form is fine-grained near the border and sends small veins into the adjoining spherulitic shell. These veins are so small as not to be visible upon a polished surface of a hand specimen even with the aid of a pocket lens, but come out distinctly in the thin section. The spherulitic shell by which Paleotrochis is enveloped is composed of fibers belonging to a number of centers or lines and yet combined they appear to form one

nodule. The biconical form of Paleotrochis suggests that it originated as two spherulite sectors of which the apices were the centers from which the fibers radiated. This would seem to be the simplest way to account for the most regular as well as many of the irregular forms, but of the specimens examined I have not been able to find one that certainly originated in that way.

A number of the fossil forms with a well-marked cup in the exposed apex turned out to be flat hemispherical or thin lenticular in section, and are composed wholly of spherulitic fibers.

Although admitting much irregularity especially on account of the supposed gemmiferous character of Paleotrochis, the ones which have been considered the most characteristic of the fossil are the distinctly biconical forms. These so far as seen are chiefly granular quartz with more or less green biotite.

It is important to note also that the dark groups of green biotite occur in the interior of very irregular nodules which have ro suggestion in them of Paleotrochis. Irregular flattened lenticular masses of granular quartz with green biotite occur within the spherulites as well as about them. The green mica is found only in the most coarsely granular groups of quartz.

The following chemical analysis, made by W. F. Hillebrand, shows that the rock has the composition of a rhyolite and accords closely with the results of the microscopical study.

Analysis of the Paleotrochis-bearing rock of Sam Christian Mine.\*

SiO,	79.57
TiO <sup>2</sup>	.11
Al.Ö	11.41 with a very little P.O.
$Fe^{2}O^{3}$	•20
FeO	.70
MnO	none /
CaO)	
SrO {	•21
BaO	•05
MgO	a very little
К.О	3.52
Na.O	3.46
H.O below 105°	.18
" above "	·61 (ignition)
	· ·

#### 100.02

Recognizing the Paleotrochis rock as an acid volcanic full of spherulites, it is easy to understand the great variation in the form of the nodules. Such rocks are in many places distinctly banded and were long considered siliceous sediments, but by

\* No other constituents looked for.

the investigations of Wadsworth, Williams, Bascom and others it has been definitely settled that they are all acid volcanics. These rocks in North Carolina are regarded by Mr. Holmes as pre-Cambrian and since their eruption may have undergone great changes like those of the South Mountain described by Miss Bascom. Some of the supposed fossils are certainly spherulites, and all of them may have been originally. Some broken forms show motion in the mass after the spherulites were developed. That Paleotrochis where most perfectly developed and composed of granular quartz is the result of deposition, after the spherulitic growths about it and within it had developed, there can be no question, but whether this deposition followed soon after that of the spherulites in the course of solidification or took place in hollow spherulites (lithophysæ). or resulted perhaps long subsequently at the time of rock alterations, is not so clear. All this and much more will doubtless be cleared up by the members of the Geological Survey of North Carolina, who were the first to correctly identify the rock and the character of the supposed fossil.

None of the Mexican specimens received from Prof. Williams were cut for microscopical examination. Some of them were clearly of igneous origin, and contained amygdules. The Paleotrochis-like forms with radial markings appeared to be composed of secondary quartz and probably originated as those of North Carolina.

About a year ago bi-conical forms like Paleotrochis were presented by Mr. Kochibi, Director of the Geological Survey of Japan, to the U.S. Geological Survey. These specimens are now in the National Museum, and are much more regular in form, size, and general appearance than the Paleotrochis of North Carolina. They are of a pale pink color with regular bi-conical, striated forms, and in some cases have shallow pits in one of the apices. They are known in Japan as "Soroban ishi" or abacus stones. One of these specimens contains a small fragment of the rock from which these curious specimens were obtained, and it appears to be spherulitic. According to Mr. Willis, who obtained the information directly from Mr. Kochibi, "these stones are found only in rhyolitic tuffs. They not infrequently occur much larger than these specimens, possibly up to two inches in diameter or more, and are more frequently associated in groups of two or three overlapping or coalescing. They are generally white, the rosy tint of these specimens being a rare characteristic." A thin section of one of these "abacus-stones" shows it to be an agate of which the outer layers are pink and the inner white. There can be no? doubt in this case that the form resulted from the filling of the cavity long after the solidification of the igneous material.

U. S. Geol. Survey, Washington, D. C., March 3, 1899.

O. A. Derby—Association of Argillaceous Rock, etc. 343

# ART. XXXVIII.—On the Association of Argillaceous Rocks with Quartz Veins in the Region of Diamantina, Brazil; by ORVILLE A. DERBY.

In a recent excursion in the region about Diamantina, Minas Geraes, Brazil, the frequent association of the decomposition products of argillaceous rocks with the quartz veins with which the underlying metamorphic series of the district is threaded attracted attention. The phenomenon was the more striking because of its absence in a long stretch of road over a newer series in which quartz veins are equally if not more abundant.

The most frequent appearance is that of a selvage to the veins and of intercallations in the mass of the quartz of a reddish foliated clay apparently resulting from the decomposition of a micaceous rock. Less prominent in the surface exposures but quite frequent in the artificial openings that have exposed the inner portions of the veins, are nests and stringers of a structureless white clay (kaolin) that may be either farinaceous or indurated (lithomarge). The red clay was observed in a sufficient number of instances to warrant the assertion that it is a general, if not a universal, feature of the quartz veins of the region and that when it occurs it is constant throughout the entire extension, both lateral and vertical, of the vein. The distribution of the white clay, on the other hand, is patchy and considerable portions of a vein in which it is known to occur may be free from it.

A magnificent exposure of a vein of this character is afforded by the eastern wall of the great cutting of the diamond mines of São João da Chapada, of which an excellent view, reproduced from a photograph, is given in Boutan's monograph on the diamond (Encyclopèdie Chemique de Fremy), and in a recent paper by the present writer in the Journal of Geology (vol. vi, p. 121). Contrary to the description previously given, based on a rapid examination made under unfavorable circumstances and with a limited experience in the identification of decomposed material, this cutting is made along the junction of a conglomeritic diamond-bearing quartzite, and an older fine-grained quartzite (itacolumite), both being profoundly decomposed and in many places indistinguishable except on the closest scrutiny. The eastern wall, which on account of its inaccessibility in the wet season, when it is defended by a frontage of quicksand, and of its superficial staining from the highly-colored overlying soil-cap has been described as a complex of various schists, proves to be a uniform mass of itacolumite with only a single argillaceous member that presents in a striking manner the above-mentioned association with vein quartz. Throughout the entire length of the cutting, a distance of over 500 meters, runs a sharply-defined layer from 1 to 2 meters thick of argillaceous material with quartz which has received from the miners the name of *Guia* (Guide), because, as they state, diamonds were to be looked for below (or in front) and not above (or behind) the outerop of this layer.

This layer consists principally of a mass of dark red foliated clay which is evidently a decomposed schist stained with oxide of iron. In several places that afford access to its interior, the central portion is seen to be occupied by an irregular but apparently continuous mass of vein quartz, that sometimes swells out so as to occupy half or more of the thickness of the layer, being in other places reduced to a thickness of a few centimeters only. Associated with the quartz is a pure white granular kaolin which in places is intimately mixed with small angular granules of quartz in a way that suggests a decomposed granite, but in general forms pockets or a selvage in or around the more massive portions of the vein. Outside of the kaolin, when this forms the marginal portion of the vein, or inclosed as angular fragments in its mass, is a minutely banded reddish, or yellowish, micaceous clay that appears to differ from the red clay composing the greater part of the mass of the Guia only in the absence of the intense staining with oxide of iron. The relations of the white kaolin with the banded clay is well shown on the scraped surface of a block that was brought away, and represented about one-fourth the natural size, in the accompanying figure, in which the dotted



portion represents the granular white kaolin and the shaded portion the banded clay. The unshaded streaks in the latter are also of white kaolin that differs from that of the vein in the less distinct granulation, but which in places, as at the lower right hand side, appears to be flame-like apophyses from it. A very pure specimen of the granular kaolin kindly analyzed by Dr. Hussak gave: SiO<sub>2</sub> 44.96 per cent,  $Al_2O_3$  42.09 per cent,  $H_2O$  13.25 per cent. This composition differs from that of a typical kaolin derived from a feldspar only in a slight excess of alumina which may perhaps be due to the precipitation with it of rare elements that are known to occur in the elay.

The quartz and kaolin are so blended that they must be considered as constituting a single geological body, and this can hardly be else than a rock of original granitic, or rather pegmatitic type. Moreover this body from the character of its contact, as shown in the figure, must have been eruptive. The character of the accessory elements is in accord with this view. Those that appear macroscopically are rare prisms of red rutile and handsome tabular crystals and groups of specular iron. The heavy residue obtained by washing is in parts very small, in other parts (where rutile abounds) very abundant, and with the appearance of being wholly authigenetic. It consists principally of rutile partly in rather large sagenitic groups of octahedral form that are evidently pseudomorphs after some mineral of the regular system (possibly titaniferous magnetite) with extremely rare grains of anatase, magnetite, tourmaline and xenotime. The latter is in beautiful glassy prisms with short pyramidal terminations of rather large size that show a tendency towards crystals of macroscopic dimensions such as occur rarely in the concentrates of the mine. The rutile and anatase are evidently secondary, and of the presumably primary accessories, magnetite, tourmaline and xenotime, the latter is the most significant as thus far it is only known in situ, at least in Brazil, as an extremely constant and characteristic accessory of the ultra-acid (muscovite) granites and pegmatites. The absence (at least apparent, as in order to avoid admixtures only small quantities could be washed) of its almost constant companions, zircon and monazite, is noteworthy. In this connection it may be recalled that in a recent paper by Dr. Hussak,\* on an auriferous quartz vein in the same series near Ouro Preto, these three characteristic granitic accessories were found together, and from this circumstance and from the occurrence of characteristic contact minerals the same conclusion was arrived at, viz.: that the vein is an ultra-acid phase of a granitic apophyse.

The colored elays of the Guia present the appearance of the decomposition products of a micaeeous schist. As already stated, the distinct banding of white and colored portions, such as is represented in the figure, in the parts next to the quartzkaolin vein, is probably due to minute interlaminated projec-

\* Zeitschr. f. prakt. Geol., Oct., 1898.

tions from the latter, and in support of this view is the fact that the white bands are distinctly kaolinitic (though not granulated like the kaolin of the vein), while the colored ones are as distinctly micaceous. Aside, however, from these distinct white bands, there is an obscure lamination visible even in the most highly-stained portions. On a carefully scraped surface cut transverse to the lamination a few scattered rounded eyes of quartz are in some portions visible, which with the banded structure are very suggestive of a stretched quartz porphyry. These eyes occur both in the dark red clays and in the lighted colored ones, but are much more abundant in the latter than This fact taken in connection with the inin the former. creased staining of the clay towards the margins of the mass and the apparent lack of a physical break between the lighter and the darker colored clays may, perhaps, be taken as an indication that the original rock was more acid in the central and more basic (or at least richer in iron) in the marginal portions of the mass.

On washing, both the dark and the light colored clays give, after a considerable loss as slime, an abundant residue of white micaceous aggregates (in the case of the red clay treatment with acid is necessary) with the aspect of sericite with rare granules of quartz that appear to come exclusively from the eves. On separation of the mica and quartz by washing or the use of heavy liquids, we find an extremely abundant residue of mixed rutile and anatase (sometimes the one, sometimes the other predominating), which appear to come from original ilmenite represented by abundant black grains in the red and by rather rare, dirty aggregates of ill-formed anatase or rutile in the lighter colored clay. With the titanium minerals occur rarely minute prisms of tourmaline and prismatic fragments, rarely perfect crystals, of monazite of the peculiar type to be described farther on. All the elements of the residue are distinctly authigenetic and in this respect are in marked contrast with those of the adjoining quartzite, which with the same titanium minerals (with the exception of ilmenite) and tourmaline in perfectly fresh crystals contains an abundance of wellrolled zircons.

The Guia is thus a composite body that consisted originally of a vein, or dike, of a quartz-feldspar rock, presumably pegmatitic granite, injected into a micaceous schist that may have been originally either a sedimentary shale or a sheared eruptive. The appearance of the mass is exceedingly dike-like, but if a dike, it must have been injected along a bedding plane, or so nearly coincident with one as to simulate an intercallated layer. The characters above given of apparent porphyritic structure, absence of distinctly clastic elements, and the presence of monazite, all favor the view of an eruptive origin and appear to be of more weight than those of schistose structure and apparent interbedding with the quartzite which are the most important that can be cited in favor of the opposite view. This question will be discussed farther on.

For an attempt to reconstruct the original rock of the colored portion of the Guia we have the positive indications of a schist free or nearly free from quartz and rich in sericite (or a micaceous mineral resembling it which for convenience will be called by that name), with an abundance of iron and titanium minerals, tourmaline and monazite, as characteristic primary accessories and with an entire lack of distinctly clastic elements which in a series with the degree of metamorphism of that about Diamantina could only be rolled zircons or regenerated tourmalines.\* For the purpose of attempting such a reconstruction, specimens were collected of such rocks as from their general aspect might be suspected of representing the original type from which the Guia clays might be derived. From the numerous specimens examined from various localities, the comparative freedom from quartz and the abundance of sericite, of iron and titanium minerals and of tourmaline prove to be common characteristics of the phyllites of the region, which can only be distinguished as presumably original sedimentaries or eruptives by the presence or absence of distinctly rolled zircons (often of a size and abundance that seems extraordinary in rocks presumed to represent fine-grained sediments) and of monazites or zircons, or both, with the aspect of original primary accessories.

The rock which from its position and aspect seemed to be the most promising was a partially decomposed greenish schist found in loose blocks at the foot of the western wall of the cutting, and which, judging from appearances, was thought to have fallen from a layer somewhat similar to the Guia and only a few dozens of meters below it in the same geological series. This, however, proves to be characterized by an abundance of well-rolled zircons and of regenerated tourmalines and by an entire absence of monazite.

Another rock from the immediate vicinity and presumably from the deep rock cutting (mainly in hard itacolumite) for the drainage canal of the Duro mine (seen in the background of the above cited figure in the Journal of Geology), is a thor-

\* See Derby, On the accessory elements of itacolumite, etc., this Journal, March, 1898. In this paper it was suggested that the lazulite that occurs quite frequently in the quartzites about Diamantina might have been derived from original clastic phosphates. This view is confirmed by an examination of more abundant material in which distinct but partially altered and corroded monazites and xenotimes were found in the heavy residue of nodules rich in secondary lazulite.

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oughly sound, bluish, imperfectly laminated phyllite of which numerous blocks have been built into a wall at the mine-house. Some blocks have in the joint planes handsome plates of specular iron like those of the Guia clay. The rock is for the most part mottled with large yellowish blotches suggestive of enclosed crystals or pebbles, and on a polished cross section shows a minute banding with sheared eyes, corresponding to the blotches, suggestive of a sheared porphyritic rock. The most massive specimen shows evidence of shearing in two planes nearly at right angles to each other, and, in this, part of the original structure which, in the most of the specimens, has been obliterated by the two systems of shearing can still be observed. The appearance under the lens is that of an altered diabasic rock sheared to the point of obliterating the rectangular outlines of the feldspars without completely destroying them. The spots above referred to have the aspect of phenocrysts of feldspar that have lost something of their sharpness of outline. Microscopic sections show a general sericitic mass blackened in irregular bands and patches with a fine dust of iron ores which on being dissolved with acid leave whitish aggregates of a titanium mineral (anatase?). The heavy residue consists of a great abundance of iron and titanium minerals, the latter only rarely showing well-defined forms of rutile and anatase. The only other elements recognizable are rare grains of tourmaline and small prismatic fragments, rarely perfect crystals, of monazite. Some of the grains referred to this mineral may possibly be zircon, but if so they are perfectly fresh (not rolled), but indistinctly characterized. The original rock was apparently a basic eruptive very rich in iron and titanium minerals (ilmenite ?) and with rare phenocrysts of the more acid element. So far as can be made out, this rock would on decomposition give exactly the characters of the red clay of the Guia. The principal difficulty in the interpretation of this rock and of the red clay of the Guia as a sheared and metamorphosed basic eruptive is the presence of monazite, which thus far is only known in situ in the acid eruptives or their metamorphosed representatives.

Two other rocks from the same region present certain characteristics in common with the one above described and if, as seems probable, they can be genetically connected with it, will serve to establish a graduation into a more acid type on the one hand (thus removing in part the difficulty above noted), and on the other hand into a better-defined basic type. From near the Serra do Gigante, several miles to the northward of São João da Chapada on the road from Diamantina to Grão Mogol, my friend and companion, Dr. Francisco de Paula Oliveira, brought a loose block of a peculiar cyanite-phyllite

## Rocks with Quartz Veins in Brazil.

full of enormous crystals of cyanite in an imperfectly laminated groundmass of sericitic appearance. The rock is free from iron ores, but extremely rich in minute aggregates of rutile and of extremely minute prismatic needles that are referred to monazite. The original rock was évidently a highly aluminous (feldspathic) one, with an abundance of a titanium mineral (ilmenite?) and of monazite, in which through shearing and the development of secondary minerals, all traces of the original structure has been obliterated. A very similar rock, but lacking the monazite, was found by Dr. Hussak on the Ilha do Fogo in the river São Francisco in front of the town of Joazeiro, where it presents the aspect of a dike in gneiss.

Some 15 or 20 miles to the southward of São João da Chapada, near the fall of the river Dattas close by the town of Gurvêa, another imperfectly laminated phyllite was found outcropping in the road that strongly resembles that of São João but differs principally in the absence of monazite, in the preservation of the original rectangular outlines of the white mineral transformed into sericite, and in the great quantity of tourmaline that is evidently an element introduced in the metamorphism of the rock. In addition to the fine iron dust that on removal by acid leaves a dust of formless aggregates of titanium, the rock contains magnetite in considerable-sized grains and octahedral aggregates of an altered titanium mineral that strongly resembles those of decomposed perofskite described by Hussak from the diamond gravels of Agua Suja (Neues Jahrb., 1894, ii, p. 297). Judging from the sharply cut rectangular outlines of the areas of sericite free from the iron dust, the original rock must have been largely composed of lath-shaped crystals like those of the plagioclase or melilite of diabasic or basaltic rocks, and with this conclusion the great abundance of the iron and titanium dust, that may be presumed to come from original ilmenite, and of magnetite with an octahedral titanium mineral, is in accord. The shearing has not been sufficient to obliterate the form of the white element and appears to have been anterior to the introduction of the tourmaline that lines the joint planes and has invaded many of the rectangular sericitic areas without passing beyond their limits.

There can be no reasonable doubt but that the rock last described is a metamorphosed and moderately-sheared basic eruptive and when it is recalled that "mixed dikes" have been described (see Zirkel, Petrographie, i, p. 784) in which a granite-porphyry passes to a type that has been described as diabase or melaphyre, the hypothesis that the two rocks above described and the decomposed material of the Guia may be genetically related is not so extravagant as at first sight appears. The most serious objection to bringing the Dattas rock into line with the others is the absence of monazite, but in regard to this it may be noted that this mineral (like the xenotime in the white kaolin) is so rare that it failed to appear in some of the tests made.\*

The association of argillaceous material with quartz veins is also a prominent feature in the diamond mines about the little village of Sopa, about a dozen kilometers to the southward of São João da Chapada. The diamond-bearing material is here a decomposed conglomeritic quartie entirely similar to that now on view in the mines of São João. + This rests unconformably on an older series of quartzites (itacolumites) with intercallated schists that is also profoundly decomposed. This lower series is abundantly threaded with small irregular quartz veins that frequently show included pockets and stringers of indurated kaolin and almost invariably partings and selvages of various colored schistose rocks or clays that closely resemble those of the Guia above described. The white kaolin which is less abundant and constant than in the Guia, affords the same residue of rutile and anatase with rare prismatic grains of xenotime. In a washing from the kaolin of the Bambá mine the residue, consisting almost exclusively of anatase with some grains approaching a macroscopic size, was nearly 0.05% of the quantity washed. In another from Misael's mine the residue is scanty, as in the greater part of the tests from the Guia, and consists principally of rutile with rare grains of anatase. In both the xenotime is in rare individuals, mostly in fragments, of comparatively large size showing a tendency to assume macroscopic proportions.

The schistose accompaniment of the veins at Sopa is, in the few cases observed in which it is well preserved, a well laminated, almost papyraceous, micaceous greenish schist that gives on decomposition an ash-colored, or reddish, clay, not distinguishable, except by its residue, from the clays derived from

\* Owing to this circumstance, and to the difficulty of avoiding admixtures, the tests of the material from the Guia in which the rare accessories proved to be infrequent and inconstant, were many times repeated and with special precautions. The identification based on form, optical properties and behavior with heavy liquids was confirmed by microchemical tests for phosphoric acid and for cerium and yttria.

+ The question of the diamond in these deposits will be discussed in another place. The conclusion presented in former papers, that the gem occurs in vein material, was based on the examination of a transs shown me in 1830 as a diamondbearing body, but which I am now convinced was a detached section of the Guia, in which, according to the best obtainable information of the present day, no diamonds have been found, and which presents no evidence of having been worked. On the other hand, it is certain that one of the diamond-bearing bodies not now visible was closely similar to it in appearance, though perhaps not in original character and origin. The section of the Guia examined in 1880 was much richer in tourmaline than the parts washed on the recent visit.

the phyllites intercallated in the series in which the veins occur. A large "horse" left standing in the center of Misael's mine, and decomposed to a yellow ocherous clay, shows to the naked eye abundant pyrite (altered to limonite) and tourmaline, and affords on washing a very slight residue of quartz, much tourmaline in handsome prisms, and a comparative abundance of well-rolled zircons with rare grains of rolled rutile and still rarer ones of sagenite that, like the tourmaline, appear to be authigenetic. An ash-colored clay poorly exposed, only a few meters away and of very similar aspect, affords an entirely different residue characterized by an extraordinary abundance of minute sharp-angled prisms of monazite of peculiar type, with rare tourmaline and still rarer octahedral xenotimes often intergrown with zircon but altered to a vellowish mass that is difficultly distinguishable from the aggregates of titanium minerals so abundant in the various rocks of the region. There is here a complete absence of rolled zircon or of other elements that can be considered as allothigenetic. Specimens from two distinct outcrops of the green schist associated with quartz veins in the immediate vicinity of the mine show, along with much rutile that is evidently of secondary origin, a mixture of the characteristic elements of the two clays above described, that is to say, perfectly sharp crystals of monazite with well rolled zircons, both in considerable abundance. A polished cross-section of one of the more massive pieces of this schist shows a banded structure with alternations of a dark green with an ash-colored material. The two are so intimately interlaminated that they could not be completely isolated so as to give perfectly unmixed residues, but there is an evident concentration of monazite in the green and of zircon in the lighter-colored portion. Thus both the character of the residue and the aspect of the specimens indicate that this schist has been produced by the shearing and metamorphism of a mass of mixed material of which one part, corresponding to the "horse" of the neighboring mine, is characterized by allothigenetic zircons and the other, corresponding to the other clay of the mine, by authigenetic monazite. Thus the veins at Sopa appear to be highly-sheared bodies essentially identical with the Guia but more completely mingled with the adjoining rocks.

The observations above recorded indicate the presence in the older series of the region of dikes of a rock characterized by titanium minerals and monazite as primary accessories that have been sheared and metamorphosed together with the rocks into which they were injected, and that the schistose and presumably weak layers thus produced have more frequently than others been the seat of subsequent injections of pegmatitic material that passes to pure quartz. In the cases examined

the material of the supposed dikes is characterized, with the single exception of the Dattas rock, by the mineral monazite which, so far as at present known, may be taken as peculiarly characteristic of granitic magmas. The original dikes may therefore be presumed to have been acid porphyries, or basic phases of such porphyries. If, however, this conclusion is correct, all eruptives of whatever nature existing in the series previous to the uplifting and shearing must have suffered a similar change and afforded planes of weak strata favorable to the subsequent injection of pegmatites, or of other types of eruptives. In the overlying series to which the conglomeritic diamond-bearing deposits examined belong, the quartz veins observed show none of these characteristics and appear to be ordinary veins of segregation. The same is also the case with the very numerous and large veins observed along about fifty miles of road over a newer series of graywackes, slates and limestones in the region lying immediately to the west of the gold and diamond section of the Serra do Espinhaco. On the other hand, a number of scattered observations indicate that the veins of the gold-mining districts of the Serra do Espinhaço present characteristics similar to those of the diamond district and difficultly reconcilable with the current hypotheses of a purely segregational origin. In the only one that has been critically examined, that of Passagem near Ouro Preto, Dr. Hussak, as already referred, has found characteristic granitic accessories and contact minerals in a great sulphuret vein, and as the somewhat similar veins of the Pary and Morro Velho mines carry garnets in the one case and microscopic zircons in the other, it may be suspected that they will on close examination, for which material is unfortunately not at hand, give a similar result. Dr. Hussak has also shown in his various papers in the Mineralogical Magazine, on the remarkable association of minerals in the cinnabar-bearing gravels of Tripuhy, that these carry monazite and xenotime, the latter of the same type as in the Diamantina district, along with the curious titanoantimoniates of which one has been traced to a sericitic schist very similar in appearance to that above described, and to a pyritiferous sericitic schist found in place in the immediate vicinity in which rare prismatic fragments of monazite of the Sopa type were detected. Lithomarge with other peculiar clays are, with quartz, characteristic features of the topaz and euclase-bearing veins near Ouro Preto, and lithomarge is a constant accompaniment of the peculiar gold and iron-bearing jacutinga veins (?) in the iron ore beds of the same region. Thus the association of argillaceous materials with quartz veins is wide spread and varied in its occurrence, and the observations here recorded are suggestive of the necessity of a careful revision of the current hypothesis regarding the segregational origin of many of these veins.

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Both the monazite and the xenotime of the clays and rocks above described and of the concentrated washings of the mines to which they have contributed, present peculiarities of form that distinguish them from the types that have hitherto been found in place in Brazilian, or other, rocks. The monazite crystals are invariably in elongated prisms with only the pinacoid plane developed giving forms that exactly resemble simple prisms of zircon with broken terminations. The extremities are most frequently broken, but occasionally one or two terminal planes are observed as in the accompanying figure kindly drawn by Dr. Hussak. The smallness of the extinction



a (100), b (010), x ( $\overline{1}01$ ), w (101).

angle  $(1^{\circ}-4^{\circ})$  increases the resemblance to zircon, which is so close that only by chemical tests and the measurement of the angles (for which material of sufficient size was fortunately found in the diamond concentrates) could their true character be determined. The xenotimes are invariably elongated prisms with pyramidal terminations in strong contrast with the octahedral type, which is the only one hitherto found in the numerous rocks containing the mineral that have been examined. The crystals when perfect are as transparent and lustrous as zircons, but are quite subject to a milky alteration and are extremely brittle. They rarely sink to the extremely minute size of the generality of the monazite crystals and show a tendency to assume macroscopic proportions. Brown opaque crystals of this prismatic type up to 10 millimeters or more in length, are quite abundant in the concentrates of the mines about the village of Dattas, a few miles to the southward of the localities above described, and there can be no doubt that they come from quartz and kaolin veins like those of São João da Chapada and Ŝopa. The octahedral type which commonly occurs in the monazite bearing granites and porphyries, and which was actually found in one of the clays from Sopa, is comparatively rare in the concentrates examined from the Diamantina region, but is abundant and of macroscopic proportions in those from the Lençoes region in Bahia. Perhaps its tendency to alteration noted in the Sopa clay may explain its rarity.

Since the above was written I am enabled, through the extreme kindness of Profs. Clarke and Hillebrand of the U.S. Geol. Survey, to add the following very minute and painstaking analysis of the peculiar rock from the Serra do Gigante, which, as indicated in the above discussion, is the most promising for giving an idea of the hypothetical original rock type from which the various schists here described may be presumed to be derived. At my request special attention was given to the detection of rare elements of which those of the cerium group and lithia were, from a preliminary examination, presumed to be present in an abundance that failed to be verified. Contrary to expectation, the rock proves to be chloritic rather than sericitic, though, as I am informed, the petrographic examination made in Washington confirmed the opinion formed here that the appearance of the predominant micaceous element is that of a muscovite mica. Contrary to expectation also, the rock proves to be basic rather than acid, and thus the principal difficulty in the way of the attempted affiliation with the Dattas and Šão João schists of diabasic, or basaltic, aspect is removed. On the assumption, based on the complete absence of recognizable allothigenetic elements, that the original rock was eruptive, no affiliation with any known type of which analyses are at hand can be made.

Analysis of Cyanitic schist, from Serra do Gigante, near Diamantina, Brazil, by W. F. Hillebrand.

				Residue insol.
	Whole mass.	HCl extract.	$H_2SO_4$ ext.	in $H_2SO_4$
SiO	38.32	10.78	14.76	(23.56)
TiO	4.93	.10	•20	(4.73)
ZrO	.09	trace ?	?	(.09) 5
Al <sub>a</sub> Õ <sub>a</sub>	28.16	10.42	14.77	(13.39)
Feo	2.24	(1.78)	(2.24)	none
FeO	4.02	(3.21)	(4.02	66
(Ni, Co)C	•04	?	`(·04)	
MnO	•16	?	(•16)	
CaO	•32	•34	·32	
SrO	trace	?	?	
MgO	12.04	9.34	(12.04)	none
K <sub>o</sub> O	1.11	•26	(•26)	•85
Na <sub>o</sub> O	•16	(.03)	(.03)	•13
Li <sub>2</sub> O s	trong trace	strong trace	(strong trace)	faint trace
$H_{2}O, 105$	° •55	(.55)	(.55)	
$H_{2}O, 220^{\circ}$	°•45)	、	· · ·	
$H_{2}O, 310^{\circ}$	22	5.36	6.80	•66
$H_{2}O, 310^{\circ}$	$^{\circ}+6.79$			
$P_2O_5$	•47	•47	(.47)	
S	trace			
F	trace?			
	100.07	42.64	56.66	43.41

No boron, nor rare earths.

## Notes to the Foregoing Analyses.

"The bracketed figures are either assumed or follow from direct determinations in one of the other columns.

An hour's treatment with concentrated sulphuric acid is sufficient for extraction of all the soluble constituents. Probably very prolonged action of hydrochloric acid would have had the same effect. The silica from the decomposed silicates separated on rotation in the insoluble form. The lithia belongs to a soluble mineral, for but a faint trace was found in the residue. The  $P_{q}O_{s}$ is wholly extracted by dilute nitric acid; it can therefore hardly exist as monazite. Moreover, careful tests failed to show a trace of rare earths. Still the lime is quite insufficient to form apatite with all the  $P_{q}O_{s}$ .

No formula for the soluble portion can be calculated from the analyses, but according to Professor Clarke it would seem to approach in composition an impure earthy chlorite.

The insoluble residue, after treatment by hydrofluoric and sulphuric acids, contained besides a large amount of unattacked rutile, practically only silica and alumina in the proportions required for exanite. Assuming that the alkali of the residue belongs to sericite, as indicated by Professor Derby's letter accompanying the specimen, and deducting accordingly for the formula of typical muscovite (KH<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>12</sub>), the following percentages remain after excluding all 'TiO<sub>2</sub> as rutile: SiO<sub>2</sub> 19:62, Al<sub>2</sub>O<sub>3</sub> 10:24, H<sub>2</sub>O '27. Again assuming that the alumina exists herein as cyanite and deducting Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to correspond, there remains 13:66 per cent of free silica. This can hardly be opaline silica, for an hour's digestion of the insoluble residue with strong potassium hydroxide solution extracted but a fraction of a per cent of silica."

In view of the apparent disaccord in some points of this analysis with the results above recorded of the physical examination with batêa, heavy liquids and microscope, the latter has been repeated with special care and on a sufficient quantity (20 grams or more) to secure a reliable result. The presence in considerable abundance of free quartz and of rutile was fully confirmed, but no reliable trace of apatite or of zircon could be found. The former if present at all, which is doubted, must be in a proportion too small to account for more than an extremely minute portion of the phosphoric acid and lime, and the latter is certainly absent. The zirconia found in the analysis must be from some other mineral and presumably from the soluble constituents of the rock. A mineral closely resembling zircon, and like it heavier than cyanite, is completely dissolved out of a mixed residue by sulphuric acid, and in the solution very satisfactory tests for phosphoric acid and cerium were obtained, the latter being precipitated as oxalate, and verified by the Florence method in both a borax and salt of phosphorus

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bead. Isolated grains gave also a very satisfactory microchemical reaction for phosphoric acid and a somewhat doubtful one for cerium, but no definite reaction for the latter could be obtained by the blowpipe method, probably on account of the smallness of the quantity of pure material available or of some disturbing admixture. On the strength of these observations and of the close resemblance in form and optical properties with the mineral from the Sopa clay, the original determination as monazite is maintained. The Sopa mineral is undoubtedly a cerium phosphate and apparently agrees in form with submacroscopic crystals from the diamond concentrates on which the angles of monazite were verified. It appears, however, to carry some titanium and lime, and possibly this peculiar type of monazite may present peculiarities of composition. The facility with which the mineral can be isolated from the Sopa schist gave an opportunity to determine roughly, by washing, its proportion as about 0.01 per cent. It is apparently much less abundant in the Serra do Gigante rock and therefore could hardly be expected to appear in the quantity ordinarily employed in a chemical analysis. It seems probable also that this rock carries some other undetermined phosphate.

Commissão Geographica e Geologica, S. Paulo, Brazil.

# ART. XXXIX.-Goldschmidtite, a New Mineral; by WILLIAM H. HOBBS.

THE analyses of Hillebrand and the crystallographical studies of Penfield which were made in connection with the monograph of Cross and Penrose\* on the Cripple Creek Mining District have established the fact that the chief telluride ore of the district is the mineral calaverite, containing about three per cent, or less, of silver. The presence of this mineral in the ores had previously been determined by Knight+ by chemical analysis. Mr. R. Pearcet of Denver had, however, assayed an ore-bearing rock from the Moose Mine, and found it to contain gold, silver, and tellurium in proportions corresponding with sylvanite, so that he believed this mineral to be From the complex nature of the material assayed present. these results can hardly be regarded as conclusive, but to the writer they would seem to indicate at least the probability of the presence of a gold-silver telluride, richer in silver than calaverite, particularly since the output of silver from some of the mines is too large to be fully accounted for by the presence of calaverite alone. Dr. Hillebrand says:

"Notwithstanding that sylvanite has not been identified by positive chemical or crystallographical tests, the evidence of Mr. Pearce as to its presence in some portions of the district at least is entitled to consideration" (l. c., p. 133).

## Source of the Material examined.

The material which I have studied was kindly given me for examination by Mr. Gustavus Sessinghaus, a graduate of the Columbia School of Mines, and now a graduate student of the University of Wisconsin. It was obtained from the Gold Dollar Mine in Arequa Gulch, in the extreme southwestern portion of the Cripple Creek Mining District. This mine is located on the northwest quarter of Section 31. (Cf. Plate VII, l. c.) It is near the flank of Grouse Mountain. The material consists of a single small hand specimen, the matrix of which is a breecia in which fragments of granite are conspicuous. Comparison with the gneissose granite of Grouse Mountain shows that the enclosures in the rock have probably been derived from that source. The cementing material of the breccia resembles the phonolite of the region, with

\*Geology and Mining Industries of the Cripple Creek District, Colorado; by Whitman Cross and R. A. F. Penrose, Jr. 16th Ann. Report, U. S. Geol. Survey, 
 Handle Original Pt. II, pp. 1–209.

 † Proc. Colo. Sci. Soc., Oct. 1, 1894.

 ‡ Ibid., April 5, 1894.

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which it probably corresponds in composition. The fragments of the breecia are, however, only loosely consolidated, so that the specimen is crossed by numerous irregular cracks, the walls of which are coated with chalcedony.

The crystals of the mineral which is here discussed are firmly attached to the chalcedony, so that great difficulty was experienced in removing them without fracture, particularly as they are possessed of a perfect cleavage. These crystals have a rather long columnar habit with some tendency also to elongated tabular forms with reference to a plane parallel to this axis, and in one or two cases they were observed to have the arborescent forms which have given the name "Schrifterz" to the mineral sylvanite, and have been explained by twinning. The largest individual observed was only about 5<sup>mm</sup> in length and those which I have succeeded in separating from the chalcedony of the walls would average hardly 2<sup>mm</sup> in length, with a thickness perhaps a third or a fourth as much. Examination with the lens showed these crystals to be considerably modified and without striation or other distortion, and, except for their minute size, they are admirably suited to measurement. They have a perfect cleavage following the plane of their tabular development. They are seen to be often twins, the plane of twinning following the columnar axis in a direction normal to the cleavage. They are quite brittle and have a hardness of about 2, since they will just scratch the surface of selenite. The amount of material was not sufficient for a satisfactory determination of the specific gravity, but the mineral's composition as recorded below, and the comparison of it with sylvanite and calaverite, make it probable that the specific gravity is very near to 8.6. The luster of the mineral is bright metallic and the color a silver white. The streak is dull, grayish black.

## Chemical Composition.

Examined on charcoal before the blowpipe, the mineral readily fuses surrounded by the light bluish green flame which is characteristic of tellurium, leaving on the coal a white coating of tellurium oxide. A yellowish white button of gold and silver results from the fusion, as in the cases of sylvanite and calaverite, though it is much less yellow than the button obtained from the last mentioned mineral. No antimony, sulphur, or selenium could be detected.

A portion of the specimen was broken up and by careful and laborious picking out of the crystals and fragments of crystals about one-tenth of a gram of nearly pure mineral was obtained, which was analyzed and found to contain gold, silver, and tellurium, in the following proportions, the tellurium being estimated by difference : 
 Percentage composition.
 Ratio.

 Au
 31'41
 '1596

 Ag
 8'95
 '0831

 Te
 (59'64)
 '4771

#### 100.00

These proportions correspond almost exactly with the formula  $Au_aAgTe_e$ , and show that the mineral is a new species, which I propose to call Goldschmidtite, in honor of my friend, Professor Victor Goldschmidt, of Heidelberg, the inventor of the two-circle goniometer and the author of *Index der Krystallformen* and *Winkeltabellen*.

Below are given in parallel columns the estimated and the theoretical proportions of the constituents of this mineral on the basis of the formula  $Au_aAgTe_a$ :

	Calculated.
(59.64)	59.95
31.41	31.44
8.95	8.61
100.00	100.00
	(59.64) 31.41 8.95 100.00

#### Relationships with other Tellurides of Gold and Silver.

The mineral sylvanite contains the same elements as Goldschmidtite but in the proportions represented by the formula AuAgTe.\* The mineral calaverite differs in being richer in gold and is not generally credited with a definite formula, because of slight variations noted in the content of silver. The number of analyses of this mineral which have now been made renders it possible, as it seems to me, to arrive at a more definite formula than (Au,Ag)Te, which assumes an isomorphous relation between gold and silver in the compound that does not exist so far as we know. Comparison of the analyses of calaverite which are given below brings out their striking uniformity with the exception of the silver percentage, and this would seem to indicate that a mineral corresponding to the one having the highest silver percentage (3.52) may form isomorphous mixtures with one that is richer in gold or perhaps entirely free from silver. Since, however, a large proportion of the analyses contain silver in amounts approximating the maximum percentage, it is improbable that isomorphous mixtures occur with tellurides much richer in silver. The formula Au Aga Te, seems best to represent the composition of this mineral.

\* Groth, Tabellarische Uebersicht der Mineralien, 4te Auflage, Braunschweig, 1898, p. 28.

#### Analyses of Calaverite.

					Te	Au	Ag	Total
1.	California,	Genth*			55.89	40.70	3.52	100.11
2.	"	" +			(56.00)	40.92	3.08	100.00
3.	Bowlder C	o., Colo. G	enth‡ -		57.67	40.59	2.24	100.50
4.	"	**	"§.		57.32	38.75	3.03	99.10
5.	Cripple Cr	eek, Colo. I	Iillebra	.nd	57.60	39.17	3.23	100.00
6.			"	¶	57.40	40.83	1.77	1.00.00
7.	٠٠	66	"	**	57.30	41.80	•90	100.00
Ca	laverite of	formula Au	ı,A <u>g</u> <u></u> 3T	e <sub>21</sub>	57.40	39.08	3.52	100.00

Comparison of the minerals calaverite, Goldschmidtite, and sylvanite brings out the fact that Goldschmidtite is, as regards its composition, intermediate between calaverite and sylvanite and almost exactly half way between them. Together the three minerals represent an homologous series quite analogous to that which has been determined for the minerals of the humite group by Penfield and Howe.++ This will be clear from the following table :

	Te		Au	Au		Ag	
	Per cent.	Ratio.	Per cent.	Ratio.	Per cent.	Ratio.	
Calaverite	57.40	$\cdot 4544$	39.08	$\cdot 1987$	3.52	.0327	
Au Ag 5 Te	. (21 =	·4536)	$(\frac{27}{3} =$	·1944)	$(\frac{5}{3} = 0)$	363)	
Difference	2.55	0256	7.54	0388	5.09	$\cdot 0473$	
Goldschmidtite	59.95	·4800	31.44	$\cdot 1600$	8.61	·0800	
Au <sub>2</sub> AgTe <sub>6</sub>	(22 =	•4752)	$(\frac{22}{3} =$	1584)	$(\frac{11}{3} = )$	0799)	
Difference	. 2·20	.0176	<u>è</u> .99	•0336	4.79	•0444	
Sylvanite	62.15	$\cdot 4976$	24.45	$\cdot 1244$	13.40	·1244	
AuAgTe <sub>4</sub>	(23 =	$\cdot 4968)$	$(\frac{17}{3} = 1)$	(1235)	$(\frac{1}{3}) = 1$	1235)	

From the above table it is seen that the common difference between consecutive members of the series in ascending order is a gain of Ag<sub>2</sub>Te and a loss of Au<sup>5</sup>/<sub>3</sub>. For purposes of comparison the formulæ of the three minerals should therefore be written:

Calaverite	Au <sup>27</sup> Ag <sup>5</sup> <sub>3</sub> Te <sub>2</sub> ,
Goldschmidtite	Au <sup>22</sup> Ag <sup>11</sup> Te.
Sylvanite	Au <sup>17</sup> Ag <sup>17</sup> Te

The next member of the series should have the formula :

# Au12Ag23Te.

\* This Journal, xlv, 1868, p. 314.

§ Ibid., xvii, 1877, p. 117.

t Am. Phil. Soc., xiv, 1874, p. 229. § Ik 16th Ann. Report U. S. G. S., Pt. II, p. 133. \*\* Ibid. TIbid. Note.-The mineral krennerite is a telluride of gold and silver richer in silver than sylvanite, but the wide and remarkable variations in the proportions of its constituents cause it to be regarded as of very indefinite composition.

++ On the Chemical Composition of Chondrodite, Humite, and Clinohumite. This Journal, xlvii, 1894, p. 188-206.

+ Ibid.
which is a close approximation to Au<sub>1</sub>Ag<sub>2</sub>Te<sub>3</sub>. The mineral krennerite contains silver in about this proportion (19:44 per cent), but the proportions of gold and tellurium do not correspond.

## Crystallography of Goldschmidtite.

As already stated, the chief difficulty encountered in measuring the crystals has been their minute size and the consequently small amount of light reflected from their faces. A number of the better faces afforded single images of the signal so that in the prism zone, where the faces were largest, consecutive readings from the same angle showed variations of less than a minute of arc, and on the best crystal the four similar angles between prism and pinacoid were respectively :

$61^{\circ}$	42'
61	46
61	$46\frac{1}{2}$
61	47를

Considerable confidence is therefore placed in the correctness of the constant which was determined from the angles in this zone, while the values of the other constants are correct only within limits of error which are sufficiently indicated by a comparison of observed and calculated values of readings of interfacial angles. Five crystals have been completely measured and particular angles have been measured also upon other crystals.

The symmetry of the mineral is easily determined as monoclinic, and it is probably also clinohedral. The principal zones of the crystal are those of the axes c and  $\overline{b}$ , a single clinodome and a pyramid which was too small to be determined being the only faces not included in these zones. Owing to the frequent absence and the small development when present of the basal pinacoid, the angle  $\beta$  was determined from the mutual inclinations of the positive and negative unit orthodomes and found to be 89° 11'. The axial ratio  $a \cdot b \cdot c$  is 1.8562 : 1 : 1.2981. The crystal forms observed number twenty-two, and are as follows:

Zone of c. - a (100)  $i\cdot\bar{i}$ ; b (010)  $i\cdot\bar{i}$ ; m (110) I; f (210)  $i\cdot\bar{2}$ ; g (310)  $i\cdot\bar{3}$ ; t (370)  $i\cdot\bar{4}$ ; l (130)  $i\cdot\bar{3}$ .

Zone of b.— y (508)  $-\frac{5}{8} \cdot \overline{i}$ ; s (101)  $-1 \cdot \overline{i}$ ; n (201)  $-2 \cdot \overline{i}$ ; r (703)  $-\frac{5}{4} \cdot \overline{i}$ ; w (401)  $-4 \cdot \overline{i}$ ; q (801)  $-8 \cdot \overline{i}$ ; x (10°0·1)  $-10 \cdot \overline{i}$ ; v (35°0·1)  $-35 \cdot \overline{i}$ ; S (101)  $1 \cdot \overline{i}$ ; N (201)  $2 \cdot \overline{i}$ ; W (401)  $4 \cdot \overline{i}$ ; X (10°0·1)  $10 \cdot \overline{i}$ ; Z (14°0·1)  $14 \cdot \overline{i}$ ; c (001) O. Zone of d.—k (032)  $\frac{3}{8} \cdot \overline{i}$ :

The more important angle readings from which these determinations were made are as follows : W. H. Hobbs-Goldschmidtite, a New Mineral.

				Obs.	Calc.	Diff.
a	: m	(100)	: (110)	$61^{\circ} 41'^{*}$		
b	: m	(010)	: (110)	$28 \ 18$	$28^{\circ}  19'$	-1'
$\alpha$	: f	(100)	<b>:</b> (210)	$42 \ 43$	42 52	-9
a	: g	(100)	: (310)	31 55	$31 \ 45$	+10
b	: Ì	(010)	: (130)	9 57	10 11	-14
b	: k	(010)	: (032)	26 49	$27 \ 18$	-29
a	: y	(100)	: (508)	65 7	65 42	-35
.А	: 8	(100)	: (101)	54 57	54 29	+28
$\alpha$	: n	(100)	: (201)	$34 \ 13$	35 17	-64
a	: r	(100)	: (703)	31 40	31 17	+23
a	: w	(100)	: (401)	$19 \ 10$	$19 \ 35$	-25
a	<b>:</b> q	(100)	: (801)	10 3	$10 \ 6$	-3
а	<b>:</b> x	(100)	: (10.01)	7 44	8 7	-23
$\alpha$	: v	(100)	: (35.01)	2 22	2 20	+2
. α	: c	(100)	: (001)	89 25	89 11	+14
Ь	: c	(010)	: (001)	89 59	90 0	+1
b	: t	(010)	: (370)	12 53	13 0	-7
$\alpha$	: S	(100)	(101)	$55 35^{*}$		
$\mathcal{A}$	: N	(100)	$(\bar{2}01)$	34 58	36 0	-62
$\alpha$	: W	(100)	: (401)	$19 \ 18$	$19 \ 46$	-28
a	: X	(100)	(10.01)	7 48	8 9	-21
a	: Z	(100) :	$(\bar{1}4.01)$	5 49	5 44	+5
b	: k	(010)	: (032)	26 49	27 18	-29





2.



3.

Of the five crystals measured, crystal I (fig. 1) is bounded by the forms a, b, m, f, g, l, v, q, r, y, and X. Crystal II (fig. 2) is bounded by a, b, m, f, w, n, s, Z, W, and N. Crystal III (fig. 3) exhibits the combination a, b, m, c, w, n, X, N, and S.

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Crystal IV (fig. 4) is doubly terminated and represents a simple twin with the twinning plane the orthopinacoid. One of its individuals (the front one in the figure) displays the forms a, b, m, f, t, n, s, N, S, and k. The other individual differs in having only one positive orthodome (N) and the form w in place of n. Crystal V (fig. 5) is also a twin crystal, on the front individual of which are developed the forms a, b, m, c, k, and s. The other individual exhibits in addition n and lacks the basal pinacoid. A small pyramid lying between k and s I was unable to determine. All the crystals show a remarkably perfect cleavage following the plane of symmetry.

### Crystallographical Affinities of Goldschmidtite and Sylvanite.

As might be expected from its chemical relationship to sylvanite, the mineral Goldschmidtite exhibits affinities also in its crystal development. Both minerals have monoclinic sym-

metry and somewhat similar forms are developed upon them. Ten of the twentytwo forms discovered on Goldschmidtite have representatives on sylvanite. Below are given in parallel columns the crystallographical constants of the two minerals and some of the angle readings between faces of corresponding forms. It will be noted that the differences are greatest in the prism zone, where the largest

4. 5.

faces of Goldschmidtite make the error of reading comparatively small. The orientation of sylvanite is that of Schrauf, which is now generally adopted.

The axes  $\dot{a}$  and  $\dot{c}$  are each about one-seventh longer in Goldschmidtite than in sylvanite. It is to be regretted that satisfactory material is not available for the crystallographical study of calaverite. That studied by Penfield\* was so poor that he was unable to determine the crystallographical constants. He thinks the mineral is probably triclinic, with its angles somewhat similar to those of sylvanite. It lacks the pinacoidal cleavage of that mineral but is observed in twins according to the face of (101). When suitable material is available forstudy it will be interesting to see whether relations between the lengths of the crystallographical axes and the proportions

\* l. c., p. 135.

of its constituent elements, can be discovered, as has been done in the case of the minerals of the humite group.

${f Goldschmidtite}\ {f Au_2AgTe}_6$	Sylvanite AuAgTe <sub>4</sub> .
Monoclinic $\beta = 89^{\circ} 11'$	$\begin{array}{l} \text{Monoclinic} \\ \beta = 89^\circ  35' \end{array}$
a : b : c 1.8562 : 1 : 1.2981	a : b : c 1.6339 : 1 : 1.1265

Perfect cleavage (010)Common twinning plane (100)Columnar axis, c Perfect cleavage (010) Common twinning plane (101) Columnar axis parallel to (101)

		Angles.	Angles.	Diff.
a	: m	$61^{\circ} 41'$	$58^\circ~32'$	$+3^{\circ}9'$
b	: m	$28 \ 18$	$31 \ 28$	-3 10
f	<b>:</b> a	$42 \ 42$	$39 \ 15$	+3 27
8	: a	54 57	54 57	
$\mathbf{S}$	<b>a</b>	55 35	54 52	+ 43
n	<b>:</b> a	34 13	35 48	-1 35
n	: 8	20 43	19 9	+1 34
$\alpha$	: N	34 58	35 16	- 18
c	<b>a</b>	89 25	89 35	- 10
S	: N	$20 \ 37$	19 36	+1 1

#### Conclusions.

1. Goldschmidtite is a new mineral species of composition represented by the formula  $Au_sAgTe_s$ .

2. It occupies an intermediate position exactly half way between calaverite and sylvanite.

3. Calaverite, Goldschmidtite, and sylvanite form together an homologous series, analogous to that of the minerals in the humite group, the common difference being the addition of Ag<sub>2</sub>Te and the subtraction of Au $\frac{5}{3}$  in passing from any one of the series to the next above it.

4. Goldschmidtite has monoclinic symmetry with  $\beta$  89° 11', and a: b: c, 1.8562:1:1.2981. It exhibits no less than twenty-two crystal forms, most of which are in the zones of c and  $\overline{b}$ .

5. Crystallographically as well as chemically Goldschmidtite shows affinities with sylvanite, ten forms being common to the two minerals, though they are referred to axial unities of which d and c are each about one-seventh longer in Goldschmidtite than in sylvanite.

University of Wisconsin.

Clarke and Darton-Hydromica from New Jersey. 365

## ART. XL.—On a Hydromica from New Jersey; by F. W. CLARKE and N. H. DARTON.

WHILE studying the Jura-trias formation in New Jersey, one of us (Darton) found in an old "trap" quarry at Rocky Hill a hydromica, which occurred under such novel conditions that it appeared to be worthy of investigation. It is found in veins of calcite, mainly as a thin coating, and adjacent to the diabase of the vein walls. The latter consist of more or less decomposed rock, of which the principal product is a soft, dark-green chloritic material. In portions of the vein the mica extends down the cleavage planes into the masses of calcite. A considerable amount of the calcite was thrown out during the quarrying operations, but only a portion of it is covered with the mica. This portion presents the appearance of having been coated with bronze paint.

The mica occurs in minute flakes thinly matted together. Its color is golden bronze, although some portions are slightly greenish. The mineral is soft, and thinly foliated. Under the microscope it exhibits no definite crystalline form; and its optical properties, although not distinctive, suggest biotite. It appears to be biaxial, but with a very small axial angle, and it is pleochroic. When heated, it does not exfoliate. It fuses before the blowpipe, at a moderately high temperature, to a dark colored bead. The specific gravity was not determined. It is readily decomposable by hydrochloric acid. The analysis, by Mr. George Steiger, of material not free from calcite, is subjoined. In the second column of figures the *reduced* analysis is given, titanic oxide and calcite being thrown out, soda recalculated to terms of potash, and the whole adjusted to 100 per cent.

	Found.	Reduced.	Ratios.
SiO,	32.72	40.24	.671
TiO	•24		
Al <sub>2</sub> Ó,	8.41	10.34	·101
Fe <sub>0</sub> O <sub>0</sub> <sup>*</sup>	19.99	24.57	$\cdot 154$
FeO	4.24	5.21	.072
CaO	10.30		
MgO	5.51	6.78	·166
K.O	•85	2.20	.024
Na <sub>o</sub> O	•63		
CO <sub>2</sub>	8.21		
H <sub>0</sub> O at 100°	2.47	3.03	.168
$H_2O$ above $100^\circ$	$6^{+}22$	7.63	$\cdot 424$
	00.70	100:00	

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This gives, as an orthosilicate, the formula

# $(KH)_{66}(MgFe)_{24}(AlFe)_{51}(SiO_4)_{67}$ . $28H_2O$ .

It is evident, from these data, that the mica is one which has been largely, but not wholly, altered to a vermiculite; the latter term indicating a mica in which potassium has been replaced by hydrogen, and which has taken up water of crystallization. So far as the analysis goes, the condition of the water is uncertain; for it was determined in two fractions only, at and above 100°, whereas more fractions are needed for accurate diagnosis. Some crystalline water may be retained far above 100°, so that the loss above that temperature includes part of this fraction plus all the water of constitution. Apart from this uncertainty the ratios reduce easily in terms of the mica theory to the following molecular mixture:

$$\begin{array}{c} \operatorname{SiO}_4 \equiv \operatorname{KH}_2 \\ \operatorname{SiO}_4 \equiv \operatorname{Al} \\ \operatorname{SiO}_4 \equiv \operatorname{Al} \end{array} + 6\operatorname{R'''} \\ \operatorname{SiO}_4 \equiv \operatorname{R'''} \end{array} \xrightarrow{\operatorname{SiO}_4 \equiv \operatorname{R'''}}$$

Calculating with the atomic ratios A1: Fe''': 2:3, and Fe'': Mg: :3:7, we have the following comparison between analysis and theory:

1	Reduced.	(	Calculated
SiO,	40.24		40.55
Al <sub>o</sub> Ô <sub>o</sub>	10.34		10.51
Fe <sup>°</sup> O <sup>°</sup>	24.57		24.71
FeÖ	5.21		5.21
MgO	6.78		6.75
K 0	2.20		2.27
H <sub>0</sub> O, 100°	3.03	Crystalline	4.34
$H_2^{\circ}O$ above $100^{\circ}$	7.63	Constitutional	5.66
	100.00		100.00

In short, the mica consists of muscovitic and phlogopitic molecules in the ratio of 9:5.

The mineral is evidently an unusual mica, differing widely from any other hitherto described. Its very high proportion of ferric oxide is its chief characteristic, and suggests a ferric muscovite as one of the antecedent, unaltered molecules. Such a muscovite is theoretically conceivable, but is not actually known.

Laboratory U. S. Geological Survey, Feb. 18, 1899.

## ART. XLI.—Powellite Crystals from Michigan; by CHARLES PALACHE.

POWELLITE was first described by Melville<sup>\*</sup> from a specimen from the "Seven Devils" Mountains, Idaho, where it occurred associated with copper ores and garnet. This material was well crystallized and Melville was able to establish its tetragonal character and the forms c(001), p(111), and e(101). The isomorphism with the scheelite group suggested by the close agreement between the axial ratio and angles of powellite and scheelite was not fully shown, though the author says: "Small rudimentary planes appear on some crystals at the lower portion of the combination edges (111) (101), thus suggesting hemihedrism as in scheelite. Indeed the curved surface which often replaces these edges, giving the appearance of fused edges, adds greatly to the evidence in favor of this supposition."

A second occurrence of powellite, in the South Hecla Copper Mine, Houghton County, Michigan, was described by Koenig and Hubbard.<sup>+</sup> Their material was poorly crystallized and added nothing to our crystallographic knowledge of the mineral. It differed from the Idaho mineral in its paragenesis, occurring with native copper and epidote, and in its composition, having only about  $1\frac{1}{2}$  per cent of its molybdic acid replaced by tungstic acid, as against about 10 per cent in the first occurrence.

Powellite continues to be found at the Michigan locality, though in small quantities and for the most part in massive form. Through the kindness of Mr. John T. Reader, of Calumet, through Dr. L. L. Hubbard, two particularly fine crystals came into the writer's hands and their description follows.

Both crystals are removed from the matrix upon which they grew. They are perfectly free from impurity of any sort and the specific gravity of the larger one could be determined with accuracy by weighing on the hydrostatic balance. Two determinations gave 4:358 and 4:353.

The crystals are pale bluish green in color, translucent, with subadamantine luster on the crystal faces and a greasy luster on fracture surfaces.

The larger of the two crystals is a centimeter in height and has one end complete, but the faces are somewhat uneven; the smaller one is half a centimeter in height and diameter and has both ends developed though neither is quite complete. The

> \* This Journal, vol. xli, 1891, p. 138. † This Journal, vol. xlvi, 1893, p. 356.

quality of its faces is sufficiently good to insure accurate measurements.

The measurements were made on a two-circle goniometer (Goldschmidt model) and the observed angles therefore appear in the form of the angular coördinates,  $\phi$  and  $\rho$ , as used in the Winkeltabelle of Goldschmidt.

The forms observed were:

p(111) e(101) h(133) j(3.11.11) k(155) l(1.11.11).

and the following table shows the observed and calculated angles.

	Symbol.		Observed angle.		Calculated angle.		No of times
Letter.	Miller.	Gold't.	φ	ρ	φ	ρ	observed.
е	011	01	00° 00′	$57^{\circ} 04\frac{2}{3}'$	00° 00′	$57^{\circ} 00'$	3
p	111	1	44 59	65 24	$45 \ 00$	65 24	2
ĥ	133	$\frac{1}{3}$ l	$18 \ 28$	$58\ 25\frac{1}{2}$	$18 \ 26$	$58 \ 26$	2
j	3.11.11	$\frac{3}{11}$	$15 \ 08$	$58 \ 00$	$15 \ 15$	$58 \ 00$	3
k	155	151	$11 \ 19$	$57 \ 38$	11 18	$57 \ 35$	1 -
l	1.11.11	$\frac{1}{11}$	$5 \ 11$	57 08	$5 \ 11$	$57 \ 11$	1

As shown by the accompanying figure, the pyramidal hemihedrism is strongly emphasized by the faces of h(133) and  $j(3\cdot11\cdot11)$ , the first especially being broad and of perfect quality. The other two hemihedral forms, k(155) and  $(1\cdot11\cdot11)$  were very narrow faces in the zone, and as they were



each observed but once they must be considered as doubtful and were therefore not introduced into the figure. There is a tendency for these planes to form a striated or curved surface between the forms p and e such as Melville observed, but there were two zones on the crystal in which the faces were sharply enough bounded to give good measurements.

The measurements lead to the same axial ratio as those made by Melville and the isomorphism of the species with the scheelite group is thoroughly established.

With the crystals of powellite sent by Dr. Hubbard was another specimen of the mineral of quite a different appearance. It consists of a rounded mass of powellite about two centimeters in diameter, upon which are a few small fragments of rocky matrix, minute crystals of bright green epidote and two or three shreds of native copper. On the broken surfaces the powellite shows an imperfect cleavage, seemingly parallel to e(101). The central part of the specimen is of the same bluish-green color as the crystals, but the surface layer to the depth of about three millimeters appears quite black and opaque in reflected light and when examined in thin splinters is seen to be colored a deep prussian blue. The boundary between the two colors is not sharp but the darker portion shades off rapidly into the lighter part.

The dark-colored material is crystallized in a number of small individuals, all in parallel position and showing approximately the same forms as the crystals before described but with greater proportional development of the forms e and h.

An attempt was made to separate some of the darker material for chemical examination, it being assumed that the lighter colored part did not differ from the similar material analyzed by Koenig and Hubbard; but it proved impossible to obtain a sufficient amount for any satisfactory tests. A small amount (051 gram) was however picked out in which there was a very slight admixture of light-colored substance and a few minute grains of epidote, and its specific gravity was determined to be 4.214. This determination is not wholly reliable on account of the impurities and the small amount of material, and it is probably too low; but it seems to the writer fairly certain that the specific gravity of the dark material is less than that of the light (4.355). The specific gravity of the pure calcium molybdate has been calculated to be 4.267 (Melville), a value which is rapidly raised by even small quantities of the tungstate. It seems probable, in view of these facts, that the dark blue material represents an occurrence of almost pure calcium molybdate. It is much to be hoped that more material will be found which will permit the chemical proof of the existence of this end member of the scheelite-powellite series.

Mineralogical Laboratory, Harvard University, February, 1899.

## ART. XLII.—The Volatilization of the Iron Chlorides in Analysis, and the Separation of the Oxides of Iron and Aluminum ; by F. A. GOOCH and FRANKE STUART HAVENS.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXXI.]

IT is well known that metallic iron is easily acted upon by an excess of chlorine at moderately elevated temperatures with the formation of ferric chloride, and that the product of the action of hydrochloric acid gas upon the metal is ferrous chloride. Out of contact with air, or moisture, both chlorides may be volatilized at appropriate temperatures-the ferric chloride below 200° C.; the ferrous chloride at a bright red heat. If water vapor, or oxygen, or air be present during the heating, both chlorides are partially decomposed with the formation of non-volatile residues, ferric oxide or ferric oxychloride.

Analytical processes involving the volatilization of iron at temperatures more or less elevated, in an atmosphere of chlorine or hydrochloric acid, have been the object of considerable attention. Thus, Fresenius,\* Drown and Shimer, + and Watts, ‡ have heated crude iron in chlorine to remove the metal and leave the non-volatile constituents; and Sainte-Claire Deville§ has employed hydrochloric acid to volatilize iron from mixtures of that metal with alumina (obtained by heating the mixed oxides of iron and aluminum in hydrogen according to Rivot), exposing the mixture, contained in a porcelain boat and placed within a porcelain tube, to the bright red heat of a charcoal furnace—an operation which was bettered by Cooke's use of a tube of platinum instead of the porcelain tube and a gas blowpipe in place of the charcoal furnace. Sainte-Claire Deville\*\* showed, further, that ferric oxide may be converted to ferric chloride and volatilized at the heat of the charcoal furnace if the current of hydrochloric acid is sufficiently rapid; but the curious effect was observed that in a sufficiently limited current of the acid no chloride whatever was volatilized, while the amorphous oxide was converted to the highly crystalline oxide of the same composition-a phenomenon which gave rise to a theory of the natural formation of specular iron in volcanic regions.

Quite recently, Moyer++ has made record of an unsuccessful attempt (in the course of experimentation upon the volatility

 <sup>\*</sup> Zeitschr. für Anal. Chem., iv, 72.

 † Jour. Inst. Min. Eng., viii, 513.

 † Chem. News, xlv, 279.

 § Ann. de Chim. et de Phys. [3], xxx, 183.

 ¶ This Journal [2], xlii, 78.

 \*\* Compt. Rend., lii, 1264.

 † Jour. Amer. Chem. Soc., xviii, 1029.

of certain chlorides at comparatively low temperatures) to convert ferric oxide completely to ferric chloride by the action of gaseous hydrochloric acid at about 200° C. At this temperature the greater part of the iron sublimed, but a residue remained, which, volatilizing neither on long heating at 200° nor upon considerable elevation of the temperature, proved upon examination to be ferrous chloride. In the experiments to be described we have acted with gaseous hydrochloric acid upon ferric oxide made by igniting the nitrate prepared from pure iron deposited electrolytically by high currents passing between electrodes of platinum in a strong solution of ammonioferrous sulphate. The oxide, contained in a porcelain boat, was heated within a roomy glass tube over a small combustion furnace. The hydrochloric acid (generated by dropping sulphuric acid into a mixture of strong hydrochloric acid and salt, and dried by calcium chloride) entered one end of the tube and passed out at the other through a water trap. In early experiments a high-reading thermometer was inserted through the stopper in the exit end of the tube so that its bulb was above and immediately adjacent to the boat carrying the oxide. In this way the actual temperatures of the vapors about the boat were fixed with considerable accuracy; later, after a little experience in gauging the effect of the burners, it was found that the temperatures could be regulated very closely without actually depending upon the thermometer. We found, as did Moyer, that ferric oxide, submitted to the action of dry hydrochloric acid gas, volatilizes partially as ferric chloride at low temperatures-180° to 200° C.-leaving ultimately a crystalline residue which does not change visibly when heated for an hour or two at 200°, or even at 500°, in the pure dry acid. According to our experience, this residue is generally slightly reddish or salmon-colored; but sometimes, especially after a second heating, the boat having been withdrawn from the tube or exposed to the atmosphere (and so to moisture), the residue is white. When it is white it dissolves in water, yields the characteristic reaction for a ferrous salt with potassium ferricyanide, gives no reaction with potassium sulphocyanide, and upon treatment in weighed amount with potassium permanganate destroys the amount of that reagent theoretically required for its oxidation upon the supposition that it is ferrous chloride. The slightly colored residue when treated with water yields a solution showing the reaction of a ferrous salt only, but when treated with hydrochloric acid and then tested shows the presence of a trace of iron in the ferric condition. Doubtless the coloration of the residue is due to an included trace of ferric oxide or oxychloride, which after exposure of the containing crystals to slight atmospheric action, is more

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easily reached in the second heating by the gaseous acid. The amount of residue is somewhat variable, but approximates under the conditions of our work to from five to ten per cent of the oxide taken: thus, in one typical experiment 0.1 grm. of ferric oxide left a residue which (withdrawn after cooling) weighed 0.0115 grm.

The greater portion of the ferric oxide volatilizes when submitted to the action of the gaseous acid at 200° quickly and abundantly in the form of the greenish vapor of ferric chloride, and if the operation is interrupted at this stage the residue which remains is nearly black, insoluble in water, slightly soluble in cold hydrochloric acid, and readily soluble in hot hydrochloric acid with the formation of ferric chloride. It is probably something analogous to the oxychloride which Rousseau\* identifies as the product of the action of water upon ferric chloride at 275° to 300°. This dark residue yields to the action of the hydrochloric acid at 180° to 200° only slowly, but ultimately only the residue which is essentially ferrous chloride remains; thereafter little volatilization occurs within the range of temperature of our experimentation—200° to 500°.

It is obvious that a reduction of iron in the ferric condition to iron in the ferrous condition takes place under the conditions of our work, and it is difficult to see how this can occur otherwise than by the direct dissociation of ferric chloride under the low partial pressure conditioned by the brisk current of hydrochloric acid gas. The temperature of formation, 180° to 200°, is far below that at which such dissociation is supposed to begin. Thus, Gruenewald and Meyert found, after cooling, no evidence of the dissociation of ferric chloride which had been heated in the Victor Meyer vapor-density apparatus to 448° in contact or partial mixture with nitrogen; but ten per cent of the residue obtained by heating to 518° was in the ferrous condition. Friedel and Crafts, thowever, did see crystals of ferrous chloride at 440° on the walls of a Dumas container filled with the vapor of ferric chloride and nitrogen, the former exerting a partial pressure of 0.75; while ferric chloride volatilized into an atmosphere of chlorine without evidence of dissociation. It seems rather surprising, therefore, to find so large a percentage of dissociation as that shown in our experiments at a temperature so low-180° to 200°. Curiously, too, we find, on repeating the experiment of heating ferric oxide in gaseous hydrochloric acid, that if the temperature of the oxide is 450° to 500° when the brisk current of acid begins to act, the whole mass of oxide is converted and volatilizes without resi-

## in Analysis, and Separation of Oxides of Iron, etc. 373

due. It is hardly to be supposed that the degree of dissociation at 450° to 500° can be less than that at 180° to 200°, and a test of the sublimate, after cooling, shows that it contains a ferrous salt. Plainly, ferrous chloride (formed by dissociation) has volatilized, and inasmuch as the ferrous chloride constituting the residue formed at 180° to 200° does not volatilize in the hydrochloric acid even at 500°, it is plain that the volatility of the former is not determined by the presence of the latter. Apparently, the cause of the completeness of volatilization must be sought in its rapidity; and this is not an unreasonable hypothesis, if one considers that an action sufficiently rapid to keep above the boat an atmosphere of ferric chloride and its products of partial dissociation, might naturally provide the very condition which would be effective in counteracting the tendency of the residue to dissociate before it volatilizes. If this hypothesis is correct, it is plain that the introduction of chlorine gas, the active product of dissociation, into the atmosphere of hydrochloric acid ought to bring about the volatilization of the residue of ferrous chloride, formed at 180° to 200°, which refuses to volatilize in the acid alone. As a matter of fact, we find by experiment that if a little manganese dioxide is added to the contents of the generator, so that the hydrochloric acid may carry with it a little chlorine, every trace of ferric oxide is volatilized from the boat at 180° to 200°; and the residue of ferrous chloride found at 180° to 200° when the hydrochloric acid is used alone is likewise volatilized at the same temperature, when the admixture of chlorine is made.

These facts, that ferric oxide is completely volatile in hydrochloric acid gas applied at once at a temperature of 450° to 500° C, and at 180° to 200° if the acid carries a little chlorine, open the way to many analytical separations of iron from substances not volatile under these conditions. In the experiments of the following table we have applied these methods to the separation of intermixed iron and aluminum oxides. The ferric oxide employed was made, as before, by ignition of the nitrate prepared from iron deposited electrolytically by a strong current passing between platinum electrodes in a solution of ammonio-ferrous sulphate.<sup>\*</sup> The aluminum oxide was made by igniting to a constant weight the carefully washed hydroxide precipitated by ammonia from a pure hydrous chloride thrown down from the solution of a commercially pure chloride by hydrochloric acid.<sup>†</sup> The hydrochloric acid

+ This Journal, II, 346.

<sup>\*</sup> The use of an anode of commercially pure iron wire naturally facilitates the operation, but in our experience the deposit thus obtained is likely to carry traces of impurity. In an attempt, too, to prepare pure ferric oxide from the oxalate thrown down out of ferrous sulphate with all precautions, the material obtained still held traces of silica, and possibly alumina, amounting to 0'0004 grm. in 0'1 grm. of the oxide.

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gas was made by dropping sulphuric acid into strong hydrochloric acid mixed with salt, and a little manganese dioxide was added when the mixture with chlorine was desired. The experimental details are given in the table.

Fe <sub>2</sub> O <sub>3</sub>	$AI_2O_3$	$AI_2O_3$				
taken.	taken.	found.	Error.	Time.	Temperature.	
grm.	grm.	grm.	grm.	hours.	⁻C°.	Atmosphere.
0.1000			0.0000	12	450 - 500	HCl.
0.2000			0.0000	1	**	"
0.1020	0.1015	0.1015	0.0000		66	66
0.2145	0.1006	0.1008	+0.0005	<u>3</u> 4	66	"
0.1000			. 0.0000	<u>3</u> 4	$180-200^{\circ}$	$HCl + Cl_{a}$ .
0.1000	0.1032	0.1035	0.0000	34	66	~ ۲
0.1072	0.1013	0.1015	+0.0005	ĩ	66	66
0.2045	0.1032	0.1033	+0.0001	11	66	66
0.1050	0.1023	0.1019	-0.0004	12	450 - 500	دد
0.2008	0.1002	0.1006	-0.0001	3	٤.	"
	0.1087	0.1087	0.0000	ĩ	66	"

The residual alumina tested in several experiments by fusion with sodium carbonate, solution in hydrochloric acid, and addition of potassium sulphocyanide gave no indication of the presence of iron.

The separation of the iron is obviously complete at 450° to 500° when the mixed oxides are submitted at once to the action of hydrochloric acid gas, or at 180° to 200° when chlorine is mixed with the hydrochloric acid. Plainly, the extremely high temperatures employed by Deville are unnecessary if the mixed oxides are submitted at once to the action of hydrochloric acid at 450° to 500° without previous gentle heating in the acid atmosphere. We prefer, however, to use the mixture of chlorine and hydrochloric acid, not only because the temperature of the reaction is lower, but because it needs no regulation, while the danger of error arising from the liability of ferric chloride to dissociate, or from deficiency of oxidation in the oxide treated, or from mechanical loss due to too rapid volatilization, is avoided.

## ART. XLIII.—Descriptions of imperfectly known and new Actinians, with critical notes on other species, V; by A.E. VERRILL. Brief Contributions to Zoology from the Museum of Yale College, No. LXII.

Family BUNODACTIDÆ. (Continued from p. 218.)

Bunodactis inornata Verrill. Figure 39.

Actinia inornata Stimpson, 1855. Bunodes inornata Verrill, Proc. Essex Inst. Salem, Mass., vol. vi, p. 61, [27], 1869, pl. i, fig. 5.

THE type of this species is still preserved, though it has at some former period been partly dried, and is, therefore, much contracted, in a hemispherical shape. The tentacles are wholly retracted. The upper part of the wall is closely covered with rather large concave suckers, but they rather suddenly diminish in size and become confused with the deep, vermiculate, wrinkles on the lower half of the column, though some persist to near the base.

In section, there are 24 pairs of larger complete mesenteries, including two pairs of directives. Alternating regularly with these there are 24 pairs of smaller mesenteries, most of which are incomplete, but are well developed, with a small but prominent muscular pennon near the distal end, occupying a quarter or less of the breadth. The larger mesenteries have strong median muscular pennons, occupying about a third of their breadth. All, or nearly all, the septa bear large gonads. The tentacles, in transverse sections, show a stellate muscular layer, due to the strong radial supports.

The sphincter muscle is large, clearly defined, nearly circular in section.

Hong Kong, at low water mark, in gravel.-Dr. Wm. Stimpson.

### Some Actinians that incubate their eggs externally.

The next four species, described below, are remarkable for the habit of carrying their relatively large eggs attached to the body in special pits, where they are retained until hatched and provided with tentacles. In these cases the egg develops directly into an actinula. This habit was described by me in 1869 as occurring in two of these species, but it has not attracted the attention of others to any great extent. I am now able to add two other species, of large size, having the same habit in a still more striking degree. They belong to the Bunodactidae, but differ considerably in generic characters.

## Pseudophellia, gen. nov. Type, P. arctica Ver.

Column much elongated, covered with an adherent cuticle, much as in *Phellia*, except near the summit. When the cuticle is removed the surface is finely papillose and wrinkled, in alcohol. Below the middle there are several transverse rows of large pits for carrying eggs. These are deeply excavated in





the wall by a thinning of the mesoglea. Capitulum smooth Wall thick and firm. Sphincter muscle well developed, circumscribed. Mesenteries form about 24 perfect pairs with a few imperfect ones. Two siphonoglyphs and two pairs of directives in the type. Tentacles tapered, in two or more rows.

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#### Pseudophellia arctica Ver. Figure 34 (type).

Phellia arctica Verrill, Proc. Essex Inst., vol. v, p. 328 [14], 1868; Trans. Conn. Acad., i, p. 490, 1869 (not of Danielssen\*).

The type of this species is still preserved. The original description is pretty complete as to the external appearance, but a typographical error occurred, in the measurement of the eggs. They are 05 of an inch in diameter (not  $\cdot 5$ ). When I originally described them I did not feel certain that they were not parasitic structures, but subsequent discoveries have removed this doubt. The mouth has two strong siphonoglyphs and about 18 folds on each side. The stomodæum is strongly plicated. There are about 24 nearly equal pairs of perfect mesenteries, with a few small ones of the fourth cycle. The longitudinal muscles are rather thick and strong on the perfect mesenteries.

The tentacles are rather large and moderately long; they are only partly retracted in the type, but the sphincter muscle is well developed, so that they are probably capable of complete retraction and concealment. In section the sphincter muscle has an ovate outline. The wall is rather thick and firm with a thick mesoglea, except in the capitulum, which is smooth externally and forms a distinct submarginal fold and small fosse. Circular muscular layer of the wall is well developed. The cuticular layer is thick and soft, and often nearly or quite conceals the eggs when enclosed in the pits, which are largely excavated in the mesoglea.

### Epiactis prolifera Ver. Figure 25.

Trans. Conn. Acad. i, p. 492, 1869. Epiactis fertilis Andres, op cit., p. 363, 1884.<sup>4</sup>

The figures now given are from one of the original types.

The largest specimens seen have about 96 tapered tentacles; they can be entirely retracted and concealed.

The wall, in section, is moderately thick and firm, with the different layers very distinct; the ectoderm is rather thick and close; muscular layer well defined and continuous. The sphincter muscle is large, clearly circumscribed, ovate in section, essentially endodermal, but not so much detached from the wall as usual in *Bunodactide*. There is a distinct collar and fosse, in contraction. The mesenteries are regularly hexamerous, in four cycles, with some small ones of the fifth; 12 or

<sup>\*</sup> The Phellia arctica Dan. (Actinida, p. 54, 1870) is a true Phellia and may be called P. Danielsseni, to avoid confusion with our species. + Andres changed the specific name on account of its prior use for Gonactinia

<sup>&</sup>lt;sup>†</sup> Andres changed the specific name on account of its prior use for *Gonactinia* prolifera Sars, but that belongs not only to a different genus, but to a widely dif ferent family, so that the change of name was not necessary.

more pairs are perfect and fertile. Their longitudinal muscles are not very thick, but cover most of their breadth.

The stomodæum is strongly plicated and has two large siphonoglyphs. The ovaries, in some cases, contain large eggs, like those carried on the outside. The egg-pits are not so deep as in the preceding three species and at first they are confined to the ectoderm, but as the embryos develop the pits become larger and deeper, partly by a slight invection of the wall and partly by a thinning of the ectoderm and mesoglæa so that at length they may be as deep as half the thickness of the wall, but they never become like the deep pits of the preceding two genera. No acontia could be found.

This genus resembles, in some respects, the *Paractida*, but it seems to belong to the *Bunodactida*, on account of the sharply circumscribed sphincter muscle, although the latter is not so much separated from the inner layers of the wall as usual in that family.

#### Epigonactis, gen. nov.

Large stout Bunodactidæ, with numerous large egg-pits on the upper half of the column, arranged in more or less regular rows and often crowded on the upper part, below the collar. These pits, when fully formed, are deeply excavated in the thick mesogleae and when containing eggs some of the latter may be nearly or quite covered and concealed by the tissues growing around them. In contraction there is a well-developed fold or collar covered with numerous longitudinal grooves, but without verrucæ; fosse smooth. Tentacles numerous, large, rather long, sulcated in contraction. Sphincter muscle large, circumscribed. Perfect mesenteries numerous and fertile. Eggs large. Wall firm and thick, in sections the layers are very distinct; the circular muscular layer shows, in alcohol, as a welldefined, continuous, brownish yellow layer; mesogleae thick.

#### Epigonactis fecunda, sp. nov. Figure 35.

Body nearly cylindrical, about as high as broad in contraction; base muscular and strongly adherent, not much wider than the column, or even narrower in one example in alcohol. Tentacles, in the smaller specimen, 72, stout, blunt, some of them rather long, others contracted so that they are only little longer than thick; they are retracted in most cases so that their tips project but little beyond the marginal collar but are not infolded; some of them appear to be perforated at tip, and most are sulcated by contraction. They are arranged in two or three marginal rows. Collar large and prominent, much thickened, but without marginal tubercles: fosse deep, with a nearly smooth surface. Outside of collar and upper parts of column below it are covered with intricate wrinkles and irregular vermiculate elevations, which surround and enclose numerous deep round pits, mostly closely crowded together. In most of the pits there is a large spherical egg, about  $2^{mm}$  in diameter; most of these project beyond the pits, but some are entirely concealed in the thickened integrument.

The egg-bearing pits are most numerous within 12 to  $15^{mm}$  of the collar margin, but some occur lower down. They form a conspicuous zone all around the body, in which the eggs are so crowded as to be in contact in the alcoholic specimens. They adhere firmly. Lower down on the column there are sucker-like pits in vertical rows, decreasing in size downward and mostly disappearing near the middle. They are obscured by the wrinkled surface, but become very evident where the soft wrinkled ectoderm is rubbed off.

In vertical section the wall is moderately thick and very firm both in base and column, plicated by wrinkles; the layers are easily visible with the naked eye, both in base and column; the circular muscular layer shows as a continuous yellow line. The mesogloca is variable in thickness, being thickened near the base and in the basal disk, but especially so at and below the collar, where the egg-pits occur; in this region it is very much thickened around and between the pits, but is very thin under them, so that it is very irregular and much lobulated; above the collar it is thin. The sphincter muscle is large, round or ovate in section, circumscribed and pedicellate. The mesenteries form about 36 pairs, of which 24 or more are perfect, but they are irregularly developed in the different sextants. In one case six fully developed and nearly equal pairs occur on one side of a pair of directives, while on the other side those of the fourth and fifth cycles are much smaller than the rest. The perfect pairs and most of the others bear large and broad longitudinal muscles, which are thick and strongly plicated. All or nearly all the mesenteries bear large gonads, which are so densely crowded together, in the specimen dissected, that it is not possible to separate them, or place them accurately. They contain numerous large ova similar in size and appearance to those on the exterior of the body. Color not recorded.

Height, in alcohol, about 2.25 inches  $(56^{\text{mm}})$ ; diameter 2.5 inches  $(62^{\text{mm}})$ .

East of Banquereau, off Nova Scotia, 150 fathoms, Sch. "Polar Wave," lot 37, 1878, 1 specimen; off Nova Scotia, 200 fathoms, Capt. John Rowe, lot 35, 1 specimen.

### Epigonactis regularis, sp. nov. Figure 36.

Body, as contracted in alcohol, nearly hemispherical, with the base as wide as any part. Disk and tentacles concealed. Wall firm and elastic, covered with a yellowish brown ectoderm; not much wrinkled, except near base and on collar. The collar is strong and sulcated, and also finely wrinkled transversely, giving the surface an areolated appearance. Near the base the wrinkles are transverse and wavy. On the upper half of the column there are vertical rows of large egg-pits, some of them circular and cup-shaped, others oval or egg-shaped; some of them are bordered by several small convergent lobes, others with folds, while some are widely open. They carry no eggs in the type, but are evidently used for that purpose. The wall is thickened at the collar, but thin above it; lower down it is of moderate thickness but firm; the three layers are very definite and easily visible to the naked eye, in sections, without staining ; the sphincter is large, elliptical in section, well circumscribed. The circular muscle layer is continuous and well-defined.

Tentacles about 90, stout, sulcated, rather obtuse, of moderate length, arranged in three or four crowded rows; mouth large, with two siphonoglyphs, bordered by large lobes.

Mesenteries form about 44 pairs, most of which are perfect and bear gonads. In a section, near the lower part of the stomodæum, 36 perfect pairs were counted, and most of the remaining eight, which were nearly as wide, may be attached lower down. Those next to the two pairs of directives, on each side, were the least developed. Owing to the equality in the size of the mesenteries no definite hexamerous arrangement could be made out. The longitudinal muscles are very broad, covering nearly the whole breadth of the mesenteries, thick and pleated; those of the directives are less thick, but have a second inner enlargement, near the siphonoglyphs. There are no rudimentary or narrow mesenteries between the larger ones in the gastric region.

Fishing Banks, off Newfoundland, in deep water. It was brought up on the trawl hooks of a Gloucester, Mass. fishing vessel, but no record of the precise locality was given.

## ART. XLIV.—A Preliminary Note as to the Cause of Root-Pressure; by ROBERT G. LEAVITT.

THE following suggestion is made in the hope of breaking a way toward the proper understanding of the nature of socalled root-pressure. The hypothesis here tentatively proposed seems to coördinate certain of the results obtained by Sachs, Clark and others, which after several years still stand in apparent need of explanation.

Van 't Hoff's interpretation of the exact determinations of osmotic pressures made by Pfeffer, de Vries, Tammann and others, which interpretation is generally accepted by physicists and by Pfeffer himself, though still neglected by the majority of writers on vegetable physiology, is here assumed as the basis of the discussion on the physical side. Unfamiliarity with this theory on the part of many botanists may warrant a condensed statement of its central principles.

Solutions (the term being applied to the dissolved substances, exclusive of the solvents) act in all ways, both qualitatively and quantitatively, as gases, exerting pressure against containing water, or other, surfaces by an inherent expansive force. The laws of solutions are identical in form, if "solution" be substituted for "body of gas," with the laws of Boyle, Charles and Avogadro for gases. Quantitatively considered, "dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume."

The distention of a turgid cell is then due to the pressure of organic matters in the cell sap, unable to escape or able to escape only with difficulty. The entrance of water is a consequence, not cause, of the osmotic pressure. A sufficient supply of water at hand is, to be sure, a necessary condition for allowing the osmotic force to act and push the cell-wall outwards, since the boundaries of the solvent, equally with definite membranes, limit the molecular wandering of the solution.

The movement of water up the stem of the thistle-tube, in the familiar experiment, is caused by the upward pressure of the solution against the free surface of the water; the water and the membrane below both being passive accessories in the operation. If the stem were crossed by diaphragms permeable by both water and solution, these would not constitute osmotic membranes in the sense of occasioning osmotic stress and flow of water; osmose and filtration of water would proceed through them. If the stem, however, were crossed by a membrane permeable by water but not by the solution, both would be stopped, and no exfiltration of the water by action of the confined osmotic substance is conceivable. Osmose being defined as the diffusion of a solution through a membrane, and water being in no sense a solution, "endosmose of water" is mistaken phraseology. Some other appropriate term should be employed, such as infiltration. "Osmotic pressure" is unmistakable, but it is well to keep in mind that pressure arises through failure of the solution to accomplish osmose.

Coming now to the plant-body as an osmotic machine, we may distinguish two categories of osmotic pressures with their consequent filtrations of water, according as (1) the solutions are confined within single (living) cells, or (2) the osmotic substances permeate the whole cellular system from root-tip to leaf. The first may be termed localized or intracellular osmotic pressure, the second general internal, or sap-pressure.

The difficulties involved in ascribing root-pressure to localized osmotic action of the root parenchyma are well understood, and need not be dwelt upon. Some of them seem to be obviated by attributing the phenomenon in question to general internal osmotic pressure. The root immersed in the wet soil may be compared to the thistle-tube of the common experiment. The root-surface or surface tissue will then answer to the membrane stretched over the mouth of the tube. Tracheæ, tracheids, intercellular spaces, and all parts dead or alive through which sap solutions percolate, may answer as a whole to the interior of the thistle-tube. Soil water may correspond to the water in the outer dish and sap with its contents, to water with its salt or sugar inside the thistle tube. The water in the stem of the latter, rising by reason of upward osmotic pressure on its free surface, overflows in an osmotically driven stream. The outflow from the root, when the stem is cut off, may have a like cause. In the artificial apparatus the solution washes out with the stream, and the end of the process ensues. In the case of the living apparatus stores of insoluble organic matters (as starch) are present, from . which the reduced fund of osmotic substances (as sugars) may be replenished from time to time by action of enzymes, causing periodic overflows of the kind described by Sachs. The flows would naturally decrease in volume as the stock of reserve materials became gradually exhausted.

The observations of Sachs on the effect of heat in increasing absorption, and of Clark on pressure in tree-trunks, accord well with the supposition that both kinds of phenomena are due to general osmotic sap-pressure.

The agency of osmotic sap-pressure as more or less important among several possible factors in maintaining or restoring the continuity of free water between root and leaf during transpiration, is here suggested. So-called negative pressure may probably be shown to be compatible with a simultaneous osmotic sap-pressure of considerable intensity, when the supply of water at the root falls below the demand.

Harvard University, April 14, 1899.

## ART. XLV.— A Study of Some American Fossil Cycads.\* Part III. The Female Fructification of Cycadeoidea; by G. R. WIELAND. (With Plates VIII-X.)

## Introduction.

FEMALE fruits of fossil Cycads from America have not been hitherto described. European specimens, however, have furnished two nearly perfect examples which have been made the objects of careful research and discussion during the past thirty years. In fact, the study of *Bennettites Gibsonianus* by Carruthers,<sup>3</sup> and Solms-Laubach,<sup>3,9</sup> together with Lignier's<sup>13</sup> investigation of *Bennettites Morièrie*, may well be considered one of the triumphs of modern paleobotany. As a result, the structure of the cycadeoidean seed-bearing organs is nearly as well known as that of the existing cycads.

The subject of female fructification, as far as treated before the announcement of the discovery of the corresponding male flower in Part I of these contributions, has been amply reviewed by Seward. Hence it is only necessary to state briefly that the object of this preliminary paper is to deal with several quite perfect cycadeoidean fruits as observed in certain trunks from the Jurassic of the Black Hills. These, it will be seen, are in all essential characters similar to the English, French, and Italian examples of *Cycadeoidea*, of which the best known are Cycadevidea (Williamsonia) gigas, Carruthers, and C. (Bennettites) Gibsonianus, Carr., both from the lower Greensand of the Isle of Wight, C. (Bennettites and Williamsonia) Morièrie, Saporta, from the Oxfordian of Normandy, and C. etrusca, Capellini and Solms-Laubach, from the Etruscan Necropolis at Marzabotto, the original locality of which is unknown. The American forms are so analogous to the several foregoing species as to preclude more than specific difference, and thus add one more argument in favor of the approximately synchronous existence of these highly specialized forms on both continents. Whether or not final study will permit their retention in a single genus is, however, a doubtful question that need not now be taken up; nor can the subject of the bracts and peduncles be treated in the present paper, although recent studies by Scott<sup>20</sup> make it quite certain that their investigation will furnish valuable data.

\* Part I of these studies appeared in this Journal for March of this year, and Part II in the April number following. The numbers refer to the list of papers given at the end of Part I.

### G. R. Wieland—American Fossil Cycads.

## The Fruit of Cycadeoidea Wielandi, Ward (MS.). 9

General Features.—Cycadean trunk No. 77 of the Yale collection, illustrated on Plate VIII, figure 1, is the female type of the foregoing species. It is a finely preserved example, bearing laterally, in addition to ten apparently fresh scars left by the shedding of ripened fruits, forty more or less complete seed-covered fruits, which were mature or nearly so when fossilization began. The shape of these fruits is ovoid, and their average size is from 3.5 to  $4^{\rm cm}$  in length by 2 to  $2.5^{\rm cm}$  in diameter. In both size and form, they resemble the fruit of *Cycadeoidea (Bennettites) Gibsonianus*, Carr., though the seeds are less elongate in the latter species.

The embryos of the seeds of this trunk prove to be the only important structures not present in unusual clearness of detail. Moreover, this was the first seed-bearing cycad to be described as such from American formations, as well as the one upon which these studies were begun. Hence it is made the first type of female fructification in American cycads, although other more perfect supplementary material has since been studied.

A close examination of the specimens represented in the plate affords interesting facts concerning the fruit-bearing habit of *Cycadeoidea*. In their various stages of growth, maturity, and dehiscence, the fruits are borne on short peduncles approximately of the same length, thus indicating that the mature fruit was not protruded further from the trunk by subsequent growth. Nor does there seem to be any order of maturity from the base to summit of the trunk in either direction.

In several other related trunks most of the fruits have been shed, being represented by scars only; while a few floral axes remain undeveloped or in an atrophied condition. Still other trunks of this and associated species are barren or bear embryonic fruits. The latter condition is of considerable importance, as it will permit a developmental study of the organs. The only general conclusion to be drawn at present, however, is that there was no sharply limited period when these cycads matured their flowers. Apparently there was a progressive maturity of fruits through an entire season, which was followed by several seasons of unfruitfulness.

From the characteristic form and sculpturing of the scars representing the position of the matured fruits, it would seem that the latter were shed by the parent plant with their parts intact and often with few or no accompanying bracts.

Following fructification and the shedding of ripened fruit, there was a closing up of bracts about the receptacle, with more or less obliteration. The appearance of the fruits as apparently mature on the trunk, and of the scars mentioned above, are fairly well represented in figures 1 and 2, Plate VIII. In all cases where the seeds are exposed the tips of the bracts are necessarily more or less worn or broken away.

The lateral, or proliferous, inflorescence here exhibited is noteworthy. In this respect these specialized culminant fossil types vary from all the higher existing forms which are sympodial, and partially agree with the genus *Cycas*. The latter is the most primitive living form, and has its peduncles distributed between the petioles for some distance below the apex of the trunk. Among the various species represented in the Yale collection there are none showing the sympodial type and but few flower-bearing examples which have no flowers on the lower half of the trunk, though the male trunks incline to bear the most of their flowers near the summit.

Special Organs.—As stated above, these fruits are ovoid bodies borne on short peduncles. The latter take their origin on the trunk after the manner of the petioles and terminate in an elongated receptacle. This bears laterally an involuce of slender enveloping bracts, and terminates in a "parenchymatous cushion," as termed by Carruthers.<sup>3</sup> The face of this cushion, or secondary receptacle, is flatly convex and bears two series of densely set organs, much modified according to their central or more peripheral position. The first of these are the seed-bearing stems, or essential organs, while the second are merely interstitial and quite analogous to chaff. They are termed "interseminal scales" by Lignier.

The disposition of these parts is illustrated in the longitudinal sections, figures 10 and 12, Plate IX, and in the corresponding transverse sections, figures 9 and 11 of the same plate, as well as in the several transverse sections on Plate X.

In this arrangement of densely set seed-bearing stems and surrounding scales borne on a fleshy bract-enveloped receptacle, there is a certain simulation of the flowers of *Composite*.

### Histological Structure.

The Parenchymatous Cushion.—This is composed of soft parenchyma centrally, but becomes more dense peripherally. Though no well-marked bundles have been noted, sparse and irregularly branching strands of scalariform cells apparently supply the seed stems. As there is usually a cleavage line, or zone of imperfect preservation, just at their origin, this could not be readily determined. The strands may scatter and end in the cushion. They are illustrated by Carruthers in his description of *Bennettites Gibsonianus*. Seed Stems.—These are very closely set on the cushion, and as it is difficult to separate their elements from those of the interseminal scales in the longitudinal sections, they may be best studied in transverse sections. Such a section from the middle of the fruit is shown in figures 14 and 16, Place X, where the stem is seen to consist of a central vascular bundle enclosed in an endodermis which is surrounded by a broad woody outer layer, or xylem zone, the "enveloppe tubuleuse" of Lignier.

Each seed stem is uniformly surrounded by from 5 to 6 interseminal scales. A series of transverse sections from the base to the summit shows no variation from this general arrangement, although there is a slow diminution in the diameter of the stems, accompanied by marked changes in the cell conformation of the xylem zone. In this and other species, there is often at the base a strong compression of the surrounding scales, while the xylem areas are more or less polygonal and composed of cells quite regularly subrhombic in section. Of these, from 30 to 40 may be counted radially, as shown in figure 4, Plate VIII. Towards the summit there is a constant increase in the size and regularity of these cells, which finally become quite round, accompanied by a decrease in the width of the xylem band, until at the base of the seeds it consists of but two layers of cells surrounding the central bundle, which remains constant in character.

This bundle is well illustrated in the enlarged view given in figure 15, Plate X. Centrally there are from 3 to 10 small woody elements. These are enveloped in soft parenchyma, not preserved in all specimens, and the bundle terminates in a well-marked endodermis. Such concentric bundles recall the somewhat similar structures seen in many ferns. The atrophied peduncles, or those lacking a well-marked central bundle, described by Lignier in C. (Bennettites) Morièrie, have not been observed thus far. The interesting case of bifd seed stems, or those with two central bundles within the same tubular, or xylem zone, however, rarely repeats itself in the present specimens.

It may be mentioned that while the figure of the transverse section of the seed stems, "vascular cords," given by Carruthers is a faithful one, its being cut too near the base, where there is much compression of the several elements, prevented a true conception of their significance. Only at some distance above the base does the clear differentiation of parts seen in figure 14, Plate X, appear. Judging from the transverse section by Carruthers, just mentioned, and the additional one given by Solms-Laubach, the tubular layer, or xylem zone, of *C. (Bennettites) Gibsonianus* was composed of more angular cells than in the case of the present specimen. Lignier gives a section of a seed stem from near a seed base (peduncle, figure 27, Plate II),<sup>12</sup> in which the tracheidal cord is followed by fundamental tissue, and this by a layer of cells (*assize colorée*), which is in turn surrounded by a single row of cells laterally dovetailing. This alteration at the seed bases has not been observed as yet by the writer, and no doubt must stand as one of the specific variations between the foregoing species.

Interseminal Scales .- Five or six of these commonly surround each seed stem, and rise beyond the seeds, their tips expanding to form the rounded summit of the fruit. Figure 13, Plate X, displays a transverse section of one of these organs cut near its middle height. In the case of cycad No. 77, figure 14, Plate X, the parenchyma surrounding the central vascular strand is not preserved; but the central strand, the large subepidermal cells (much less continuous in this species than in C. Morièrie), and the epidermis, are so uniformly present as to differentiate these tissues as absolutely as any staining. From the base toward the summit, as the seed stems decrease in diameter, the scales increase in size by the enlargement of the cross area of the parenchyma cells, which are usually rounded in section and quite elongate. Beyond the seeds, the cells composing the expanded summits are entirely lignified. In the seed zone, the scales are also more or less lignified and often very thin and flat as they pass between the seeds, where it is sometimes difficult to differentiate them from the seed coats. Exterior to the outer seed stems there is a flattened overlapping series of scales, forming a kind of lateral wall of the fruit several scales in depth. The distal portions of these modified scales are elongate, tetrangular, and lignified, as they appear on the fruit surface.

It is difficult to detect the several elements of the scales in longitudinal section. That some of the xylem cells are spirally marked is certain, and that there is an occasional scalariform marking is also certain. The woody elements of these scales regularly take their origin below that of the cells of the xylem zone of the seed stems, and in figure 5, Plate VIII, are seen extending down into the parenchymatous cushion as small projecting brushlike groups.

It need scarcely be pointed out that there is an analogy between these scales and the central bundle of the seed stems, the variation being in a uniformly large central strand, the addition of a broken subepidermal layer with apical sclerotization, and the presence of occasional ducts in the case of the scales.

The Seeds.—The seeds thus far observed in the present and other species show much variety of preservation. Their study is therefore a difficult one, requiring time, especially for the

AM. JOUR. SCI.-FOURTH SERIES, VOL. VII, No. 41.-MAY, 1899.

purpose of comparing a large number of the same and different species, and determining how far the structures supplement each other. Hence no detailed account of seed structure will be now attempted, although the appended figures, which in reality are but little diagrammatic, are introduced.



FIGURE 1. - Cycadeoidea (Bennettites) Morièrie, Saporta 9; longitudinal section of

a, micropylar tube; b, prismatic layer; c, pulpy tissue; d, corpuscular mass; e, interseminal scales; f, embryo space; g, remains of nucellus; h, chalaza; i, tubular layer (= xylem zone); k, micropylar canal; l, nucellar beak; m, pollen chamber; n, fibrous stratum; o, basal expansion of n; p, parenchyma of seed stem.

FIGURE 2.—C. Wielandi, Ward  $\mathfrak{P}$ ; longitudinal section of seed.  $\times$  12

a, micropylar tube; b, interseminal scale; c, the same; d, cotyledons; e, fibrous layer ending below the chalaza in an expanded base of scalariform tissue; f, a structureless zone; g, stringy remains of cells lignified and slightly expanded below; h, chalaza; i, woody scalariform tissue; k, prismatic outer layer of seed ending in xylem zone ; l, parenchyma.

### General Considerations.

Owing to the large number of male and female examples of Cycadeoidea in the Yale collection, their proper correlation will require considerable time. Nevertheless, several facts of im-

portance present themselves for mention. A number of species bear fruits of the type represented in the well-known figure of C. etrusca given by Capellini and Solms-Laubach (Plate IV).10 These heart-shaped fruits have very closely set, rodlike seeds arranged prismatically on a short, fleshy axis, traversed by numerous gum ducts and usually devoid of the regularly arranged seed stems and interseminal scales characterizing C. (Bennettites) Gibsonianus, C. Morièrie, and C. Wielandi. Should there prove to be no intervening forms and no connection during developmental stages, this must be finally regarded as a strong generic difference. One of the Yale specimens not yet fully studied, but nearly related to C. etrusca, as far as may be judged from general features, displays seeds with wellmarked cotyledons, as represented in figure 7, Plate IX. Another closely related trunk, of which the female form also is known, shows well-preserved male cones of essentially the same character as those described in Part I of these contributions. Pollen grains, both distended and dessicated, and represented in figures 9–16, are present in rare preservation. They are so like the dissociated pollen figured by Capellini and Solms-Laubach" in their description of C. etrusca that figures 17-20 in the text are introduced for comparison, as well as pollen from the living cycad *Ceratozamia*, figures 3-8. That these fossil bodies represent characteristic cycad pollen is beyond all question. Sections of the cycadeoidean cone from which the pollen of figures 9-16 was derived are given in figures 17 and 18. Plate X.



FIGURES 3-8.- Ceratozamia longifolia, Miquel; pollen grains. (After Juranyi.) × 610.

3, mature pollen in dry condition; 4, 5, the same swollen in water; 6-8, the

respective transverse sections, or end views. FIGURES 9-16.—Cycadeoidea, sp., Black Hills; pollen grains. × 250. 9, 10, 13-15, more or less desicated granns; 11, 12, 16, normal forms. FIGURES 17-20.—Cycadeoidea etrusca, Capellini and Solms-Laubach; isolated and

dried pollen grains. (After Capellini and Solms-Laubach).

# G. R. Wieland-American Fossil Cycads.

But one interpretation of these facts is possible—*Cycade*oidea etrusca represents a fertilized diœcious plant, the male flower of which has now been definitely recognized in an allied species. The so-called "antheriferous tissue" noted by Capellini and Solms-Laubach hence remains an unexplained structure, possibly of much significance. Should this tissue represent a developmental stage instead of permanent structure, as certain sections made by the writer suggest, it nevertheless merits the closest examination, and may have some connection with a "corona" such as that of Williamsonia gigas.

Another close resemblance between the American and European species having prismatic seeds is the characteristic surface sculpturing. Figure 2, Plate VIII, is introduced here for comparison with a Bennettitean specimen illustrated by Seward (Fossil Plants of the Wealden, Plate XV, figures 5 and 6).\*

Yale Museum, New Haven, Conn., April 24, 1899.

#### EXPLANATION OF PLATES.

#### PLATE VIII.

- FIGURE 1.—Cycadeoidea Wielandi, Ward  $\Im$ ; type specimen.  $\times \frac{1}{4}$ .
- left by the shedding of fruits.  $\times \frac{1}{4}$ . FIGURE 4.—Cycadeoidea turrita, Ward Q; transverse section of a seed stem
- (from near the parenchymatous cushion) surrounded by an unusual
- number of interseminal scales. × 30.
  FIGURE 5.—*Oycadeoidea Wielandi*, Ward Q; longitudinal section through seed stems, showing their origin on the parenchymatous cushion. × 24.
- FIGURE 6.—Same fruit as figure 5; transverse section of seed stems near periphery of fruit. × 30. (Compare with figure 14.)

#### PLATE IX.

- FIGURE 7.- Cycadeoidea (sp.) Q; nearly transverse section through the periphery of a fruit, cutting 5 seeds, in several of which the cotyledons may be seen.  $\times 16$ .
- FIGURE 8.- Cycadeoidea Wielandi, Ward Q; longitudinal section through a fruit near the summit, cutting superimposed seeds.  $\times$  12.
- FIGURE 9.- Cycadeoidea Wielandi, Ward Q; type specimen; transverse section through fruit; showing seeds, seed stems, and interseminal scales. ×4.
- FIGURE 10.-Same fruit as preceding; longitudinal section through seed stems and

parenchymatous cushion. ×4. FIGURE 11.—*Cycadeoidea turrita*, Ward ⊋; transverse section through fruit, cutting a single seed obliquely. ×25.

FIGURE 12.—Same fruit as preceding; longitudinal section. × 4. a, seed; b, densely set interseminal scales and aborted seed stems (?); c, the parenchymatous cushion; d, involucral bracts; e, line of dehiscence (?).

\* In the case of generic and specific names, the writer has followed Prof. Lester F. Ward of the U.S. National Museum, as the recognized authority on American cycads. Fortunately for scientific uniformity, Prof. Ward has described practically all the cycads discovered in this country.

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## PLATE X.

IGURE	13 Cycadeoidea Wielandi, Ward Q; transverse section of an inter-
	seminal scale. $\times$ 185.
	a, xylem zone of a bordering seed stem; $b$ , epidermis of the
	interseminal scale; c, xylem; d, parenchyma; e, heavy and much
	broken subepidermal layer.
	NOTE. — Where two scales border there is a double layer of $b$ .
IGURE	14Cycadeoidea Wielandi, Ward Q; type specimen; transverse sec-
	tion through seed stem and surrounding interseminal scales, no
	parenchyma of either of these organs being preserved. $\times$ 22.
IGTRE	15.—Same fruit as figure 13; transverse section through the central
	bundle of a seed stem. $\times$ 185.
	a, xylem zone; b, endodermis; c, parenchyma; d, xylem; e, cel-
	lular interspace.
IGURE	16.—Same fruit as preceding; transverse section of seed stems and
	interseminal scales, all elements being preserved. $\times$ 22.
IGURE	17.—Cycadeoidea (sp.) 3; transverse section through the pendent sori
	of a sporophyll. $\times 18$ .
	a, epidermis of prismatic cells which entirely invests each sorus,
	the latter consisting of two parallel rows of sporangia; b, one of
	the sporangia containing pollen grains as illustrated in text, figures
	7–14, page 389.
IGURE	18.—Same as preceding, but showing a larger area. The arrow points
	towards the floral axis. $\times 3$ .

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#### SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. On Low Temperature Experiments .- In consequence of the easy production of liquid oxygen and nitrogen in recent times, experiments at low temperatures have become common. HEMPEL has called attention to the fact, however, that with much simpler means than these, temperatures sufficing for the greater part of the ordinary reactions can be secured. Thus, for example, liquid carbon dioxide, now commercially very cheap, may readily be employed to show that potassium and bromine no longer react on each other at low temperatures. If the bromine be first placed in a mixture of solid carbon dioxide and ether and thoroughly cooled, and then a piece of potassium, cooled in a similar bath, be introduced into it in a small spoon, no combination takes place; though it speedily sets in as the temperature of the mixture rises. Very considerable improvements, however, are necessary in the methods of manipulation. The double-walled and exhausted globe of Dewar, therefore, has been of great service. But these Dewar globes are costly and fragile when they are of large size; and hence are not available for laboratory experiments on any large scale. The author therefore has experimented to determine to what extent a sufficient isolation can be secured in other ways. Test tubes 4cm in diameter, approximately of the same size as the Dewar tubes, were placed in beakers 13cm in diameter, the space between being packed with the material to be tested. Equal quantities of solid carbon dioxide and ether were placed in each of these tubes; so that at the beginning of the experiment all the vessels contained equal quantities of material at  $-79^{\circ}$ . From time to time the temperature in the several tubes was determined by an electric pyrometer. In 5 minutes the tube packed with cotton had a temperature of  $-76^\circ$ , that with wool  $-77^{\circ}$ , that with eider-down  $-78^{\circ}$ , and that with a well exhausted Dewar tube  $-77^{\circ}$ . After 58 minutes these values were successively  $-56^{\circ}$ ,  $-64^{\circ}$ ,  $-67^{\circ}$ , and  $-54^{\circ}$ ; thus showing that well dried wool and eider-down are very good insulators, being exceeded only by the best Dewar tubes. For preparing the solid carbon dioxide the author prefers a paper funnel with a wide short neck, to the upper edge of which is fastened a cylindrical bag of linen. On clasping the upper portion of this bag about the valve on the cylinder containing the liquid gas, and opening this valve, the solidified gas collects in the bag and may be readily shaken into the funnel. About 270-300 gms. of the solid are obtained from a kilogram of liquid; and since this liquid costs about 15 cents a kilogram, the solid would cost not far from fifty cents a kilogram. No advantage in yield was found to result on cooling the liquid before expansion. The lowest temperature is obtained when the solid carbon dioxide is mixed with

ether to a stiff magma.—Ber. Berl. Chem. Ges., xxxi, 2993-7, December, 1898. G. F. B.

2. On Reductions in Presence of Palladium.-Although palladium-hydrogen has been used already as a reducing agent by Graham and by Saytzeff, yet now by a more extended study ZELINSKY finds that it may be employed with great success in the reduction of bromides and iodides of cyclic alcohols, a class of compounds which hitherto it has been impossible to reduce by any of the ordinary methods. The form in which it is used is that of a palladium-zinc couple, analogous to the copper-zinc couple of Gladstone and Tribe. To form it, zinc filings are well washed with alcohol, then treated with sulphuric acid until an active evolution of gas takes place, and finally washed with water. On pouring upon them a one or two per cent solution of palladium chloride previously acidified with hydrochloric acid, a thin strongly adhering layer of palladium is deposited upon the zinc. The couple thus formed is washed with alcohol and dried. To effect the reduction, which takes place at the ordinary temperature and up to 100°, a flask provided with a reflux-condenser and dropping funnel is one-third filled with the palladium-zinc couple, this couple is partly covered with methyl or ethyl alcohol and hydrochloric acid saturated at 0° is run in drop by drop. At first the hydrogen is absorbed by the palladium; and as soon as bubbles of gas are evolved, the bromide or iodide to be reduced is added gradually, alternately with the acid. The action is controlled by regulating the quantities of material added. The evolved gases are passed through alcohol to retain any volatile hydrocarbon which may be carried over. The palladium-zinc in the flask, after washing with acid and with alcohol, is ready for further use .-

Ber. Berl. Chem. Ges., xxxi, 3203-5, January, 1899. G. F. E. 3. On the Properties of Metallic Calcium.—Further results have been communicated by MOISSAN on the properties of calcium. Prepared by the method already described,\* the metal separates from fused sodium in hexagonal crystals which have a specific gravity of 1.85 and melt at 760° in vacuo. On solidifying, the metal is somewhat brittle, is less malleable than potassium or sodium and shows a crystalline fracture. When free from nitride, it is silver-white in color and has a brilliant surface. Heated to redness in a current of hydrogen, a crystalline hydride CaH, is formed. When pure, calcium is not acted on at ordinary temperatures by chlorine; though at 400° the action is decided. But if the metal contains nitride, chlorine attacks it at the ordinary temperature. At 300° it ignites and burns brilliantly in oxygen. Gently warmed in air, it burns with brilliant scintillations. It combines with sulphur at  $400^{\circ}$  with incandescence. At a red heat it unites actively with lamp-black, yielding CaC<sub>2</sub>. Calcium gives somewhat brittle alloys with magnesium, zinc and nickel. With tin the alloy contains 3.82 per cent of calcium, has a density of 6.70, and slowly decomposes water. A crystalline amalgam is

\* This Journal, IV, vi, 428, November, 1898.

formed with mercury which may be distilled in hydrogen at 400°, but which forms nitride when heated in nitrogen. Heated to redness with potassium or sodium chloride, calcium sets the metal free. Water acts on calcium only very slowly, evolving hydrogen. At a red heat, it combines explosively with phosphoric oxide, and decomposes silica, yielding calcium silicide and some silicon. At 600° it reduces boric oxide to boron. Nitric acid when strong acts on calcium very feebly, though when diluted the action is rapid. Fuming sulphuric acid is reduced by the metal. Heated to dull redness in ammonia, a mixture of hydride and nitride is produced. In liquefied ammonia at -40°, calcium ammonia is formed, a reddish brown solid.— C. R., cxxvii, 584-590, October, 1898.

4. On New Bases from Strychnine.—It has been noticed by TAFEL that when a current of five amperes at a potential of three and a half volts is passed through a solution of 30 grams of strychnine in 180 grams of concentrated sulphuric acid diluted with 120 grams of water, two poisonous bases are produced which he calls tetrahydrostrychnine and strychnidine. After passing the current for two hours, the liquid, diluted with four volumes of water, is nearly neutralized with barium carbonate, filtered, heated to boiling and treated with barium hydrate in slight excess. The strychnidine is contained in the precipitate while the filtrate contains the tetrahydrostrychnine. Strychnidine crystallizes from alcohol in stellate groups of colorless needles, fusing in vacuo at  $252^{\circ}$  and having the structural formula

 $C_{_{20}}H_{_{22}}NO {\leqslant} {{}^{CH_{_2}}_{N.}} \ \, It \ \, boils \ \, at \ \, 290^\circ-295^\circ \ \, under \ \, 14^{mm} \ \, pressure, \ \, and$ 

may be distilled undecomposed, the distillate solidifying to a crystalline mass. It is sparingly soluble in water, but dissolves more freely in alcohol, benzene and chloroform. A 6.4 per cent chloroform solution has a specific rotatory power  $[a]_{p} = -8.28^{\circ}$  at  $20^{\circ}$ . Dissolved in sulphuric acid, it gives color with oxidizing agents. Its aqueous solutions with excess of acid become intensely red with potassium dichromate, hydrogen peroxide, ferric chloride and sodium nitrite. Tetrahydrostrychnine C20H22NO(NH). CH2. OH crystallizes from alcohol in colorless prisms, containing a molecule of the solvent, which it loses at 100°. It dissolves in 280 parts of water at 20°, the solution being strongly alkaline. It resembles strychnidine in its action with sulphuric acid and oxidizing agents, but gives a wine-red solution when its hydrochloric acid solution is treated with chromic acid or ferric chloride. Strychnoline, obtained by reducing dioxystrychnine in amyl alcohol with sodium, and dihydrostrychnoline, produced by passing a current through a solution of deoxystrychnine in sulphuric acid, are also described.-Liebig's Annalen, ccci, 285-348, August, 1898. G. F. B.

5. A History of Physics in its Elementary Branches including the Evolution of Physical Laboratories; by FLORIAN CAJORI,

Ph.D. 8vo, pp. viii, 322. New York, 1899 (The Macmillan Company).-In this book the author has attempted a somewhat condensed review of the progress in physical science from the earliest times to the present. In the preface he quotes Ostwald's statement to the effect that a defect attaching to present scientific education is the absence of the historical sense and the want of knowledge of the great researches upon which the edifice of science rests. It seems to be fully recognized that the historical development of a subject is an essential aid to the proper understanding of it. It may be a question, however, whether this historical treatment should not be given in connection with the subject discussed rather than have a separate course devoted to it. In this book the history of physics is divided into time epochs, i. e., that of the Greeks, the Romans, the Arabs, the Middle Ages, the Renaissance, the Seventeenth Century, the Eighteenth Century and the Nineteenth Century; closing with a chapter on the Evolution of Physical Laboratories. This method seems to necessitate considerable repetition, light for example being considered six times. Possibly a physical classification would entail less repetition and be handier for reference. A wide range of references has been made use of and these are given in foot-notes. The book will undoubtedly be of use to students and teachers of physics, for whom it was intended.

6. The Electrolytic Interrupter.-Much interest has been excited by Dr. A. Wehnelt's new interrupter for induction coils, which consists of a lead plate, the cathode, and a platinum point, the anode, immersed in dilute sulphuric acid and connected with an electrical source of comparatively high voltage. At a recent meeting of the Physical Society in London, March 10, Mr. A. A. CAMPBELL SWINTON described his experiments with this interrupter. It was found that the minimum working voltage was twenty-five volts. The spark-pitch varied with the length of the platinum terminal wire. The wire must be immersed in the dilute acid before the circuit is closed, otherwise the action is not obtained. The interrupter becomes fatigued in a quarter of an hour and then the platinum becomes red-hot. The interrupter would be very effective for X-ray work if it did not heat the Crookes tubes. Mr. Swinton suggested the use of the interrupter for the production of Hertz waves. Professor Oliver J. Lodge thought that it would not be effective for this purpose since the air would not quickly regain a non-electric condition. The interrupter will work with an alternating current but with half the efficiency, apparently allowing only one-half the alternations to pass. A well-known arrangement, however, of circuits might give a greater efficiency.-Nature, March 16. J. T.

7. Measurement of slow electrical oscillations.—W. KÖNIG discusses previous methods of receiving the sparks from an induction coil on lamp-blacked rotating discs, and describes an efficient method of measure, which consists of a tuning fork provided with a stylus which serves both to register the time on a blackened disc connected with a pendulum and to serve as a terminal to deliver the spark to the moving disc. With this apparatus he finds that he can follow changes of potential under twenty volts. He finds that the electrostatic capacity of the bobbin of the induction coil is of the order  $16 \times 10^{-12}$  farad. The working of the iron core of the coil diminished with increasing number of vibrations.— Wied. Ann., No. 3, 1899, pp. 535-562. J. T.

8. Electric waves on wires.—W. D. COOLIDGE has succeeded in photographing electric waves on wires by using a vigorous exciter—Blondlot, or Tesla transformer. The photographic lens was placed above the wires, which were horizontal. The nodes and ventral segments are clearly distinguished in the photographs. — Wied. Ann., No. 3, 1899, pp. 578-591. J. T.

9. Absorption of the X-rays by air.—Since very short ultraviolet waves of light are absorbed by air, it is an interesting question to consider the absorption of the X-rays by air. Some recent experiments by Prof. Trowbridge and Mr. J. E. Burbank in the Jefferson Physical Laboratory instituted to study this question show that the difference of absorption of a column of air thirty inches in length at atmospheric pressure and a column of air of the same length at four millimeters pressure cannot be distinguished by the use of a fluoroscope. With cathode rays the difference is as thirty-three to one. That is, the absorption is thirty-three times as much in air at atmospheric pressure as at four millimeters pressure. The electrostatic effects in the exhausted tube thirty inches long are very beautiful and cease when the concave mirror of the X-ray tube becomes the positive terminal.

10. Die Optischen Instrumente der Firme R. Fuess; deren Beschreibung, Justierung und Anwendung von C. LEISS; pp. xiv, 397, with 233 text figures and three photo-plates. Leipzig, 1899 (Wm. Engelmann).-Very important advances have been made within recent years in the methods and apparatus applicable to crystallographic and optical investigations. The present volume, giving an account of the instruments furnished by the firm of R. Fuess (Berlin), is very thorough and complete and will be of great value to all working in this field. There are described here, for example, a number of forms of spectrometers and various types of apparatus to be used with them, as, for example, the new spectral arrangement of Wülfing, giving homogeneous light of different wave lengths. The reflectometers, spectrographic apparatus, goniometers, microscopes, are also fully and minutely treated of. The chapter giving an account of the different forms of apparatus for projections with electrical lamps is particularly interesting and timely. The volume is not simply a catalogue of instruments, but gives full descriptions of the method of use applicable in each case, with references to the original papers. The worker is thus told not only what instruments are to be had, but when he is supplied with them, how they are to be adjusted and used in practical investigations.
### II. GEOLOGY AND NATURAL HISTORY.

1. Note on a Bridger Eocene Carnivore; by O. C. MARSH.\*— A reëxamination of the three species of the genus Limnocyon described by me in 1872 (this Journal, vol. iv, pp. 122, 203, and 204), leads to the conclusion that the type is in all probability to be referred to the genus Sinopa, Leidy, from the same horizon. While this statement applies to Limnocyon verus, the species first described, yet a second species of the genus, Limnocyon riparius, described by me in the paper cited, is undoubtedly distinct, and cannot be placed in any known genus of Eocene Carnivora. Since the type species of the genus, however, is thus shown to belong to Sinopa, the generic name Limnocyon must be abandoned and another substituted. I therefore propose the name Telmatocyon, basing the genus on the remains referred to Limnocyon riparius.

The generic characters may be stated as follows:

Dentition:  $I_3$ ,  $C_7$ ,  $Pm_7$ ,  $M_2$ ; two lower molars subequal in size and tuberculo-sectorial in pattern; internal cusps of these teeth considerably reduced, as in *Sinopa*; jaw very straight on inferior border, not unusually deep, but relatively thick and heavy, symphyseal portion abrupt and robust; first superior molar with external cusps well separated, and not closely approximated as in *Sinopa*.

This genus thus differs from the contemporary Viverravus, in the unreduced condition of the second lower molar as well as in the character of the jaw; from Vulpavus, in having two instead of three lower molars; and from sinopa as already indicated. 2. The Age of the Franklin White Limestone of Sussex County,

2. The Age of the Franklin White Limestone of Sussex County, New Jersey; by JOHN ELIOT WOLFF and ALFRED HULSE BROOKS, Eighteenth Annual Report of the U. S. Geological Survey, 1896– 97, Part II, pp. 425-457, 1898.—Messrs. Wolff and Brooks have made a careful study of the white limestone of Sussex County, which, with the blue limestone of the same region, has been the subject of many papers of those attempting to determine the age of the limestones. Mr. Nason, in 1890, gave at the time what seemed to be conclusive evidence of the Cambrian age of the white limestone, attributing its crystalline condition to the intrusion of igneous rocks, and also maintained that the white and blue limestones passed one into the other. The present writers have reached the conclusion that the white limestones are pre-Cambrian in age, and that the quartzite and blue limestone are Cambrian. Their conclusion regarding the relationship of these is as follows: "That the white limestone was deformed and metamorphosed to its present condition and partly eroded before the basal member of the Cambrian series was laid down; that the

\*This note was prepared by Dr. J. L. Wortman, who first called Professor Marsh's attention to the points of synonymy as here given. The matter was left incomplete at the time of Professor Marsh's death.—Ep. deformation which the area has suffered since the deposition of the Cambrian, which has manifested itself in folding and faulting, has been but slight compared with the pre-Cambrian deformation; and that the Cambrian rocks overlie the white limestone, as well as the gneisses, unconformably. As a result of our observations, we are compelled to adopt the pre-Cambrian age of the Franklin white limestone."

3. West Virginia. Geological and Economic Survey.—Professor I. C. White, the State Geologist, has issued a map of West Virginia, compiled by Russell L. Morris, C.E., on the scale of 10 miles to the inch, on which are given the location of oil pools, natural gas wells, and the approximate distribution of the New River, Alleghany or Kanawha River, and Pittsburg coal areas. The map is not complete, but is issued as a preliminary one only. H. S. W.

4. Alabama Geological Survey. Iron-Making in Alabama. Second edition; by WILLIAM BATTLE PHILLIPS, pp. 1-380, 1898.— This is a second edition of the report published in 1896, containing new statistics regarding the products of the State. Several new chapters have been added, among them additional information as to the coal industry, compiled from the report by James D. Hillhouse, State mine inspector. H. S. W.

5. The Development of Lytoceras and Phylloceras, by JAMES PERRIN SMITH, Pro. Cal. Acad. Sci., 3d Ser., Geol., vol. i, pp. 129-160, plates xvi-xx, 1898.—The two genera Lytoceras and Phylloceras are chiefly interesting "because they are simple, unspecialized genera, long-lived, little changed, and yet with the power of giving off other variable branches. They are the two longest-lived genera of ammonites, ranging from about the end of the Trias to the Upper Cretaceous, at least seven millions of years by a conservative estimate." The author has prepared beautiful plates illustrating the sutures of the protoconch and following stages of growth; and concludes from his studies that "these two genera come from a common origin, and follow the same paths up to Nannites, where they part company, each going through a stage corresponding to that genus, but to different species under it; both go through Monophyllites stages, but here again analogous to different groups and even different subgenera. There the resemblance ceases, and they develop into different families probably by the middle of the Trias, for in the upper division of that formation Megaphyllites and Monophyllites are sharply distinguished from each other. In the life-history of these two genera we have a rare opportunity of observing acceleration of development, and divergence of two nearly related stocks, whose history may be traced from the Paleozoic to near the end of the Mesozoic eras." н. ѕ. พ.

6. Pre-Cambrian Igneous Rocks of the Fox River Valley, Wisconsin; by S. WEIDMAN (Wis. Geol. and Nat. Hist. Surv., Bull. III, Science, Series 2).—This is a geologic and petrographic description of three areas of igneous rock, which appear to have been islands during the deposition of Cambrian sediments. They consist of an ancient rhyolite, a rhyolite changed to gneiss and a granite, which probably represent phases of a parent magma. The various changes induced in these rocks through mechanical deformation in two of the areas and through chemical alteration alone in the third have been carefully studied and many features of interest are developed. L. V. P.

7. West Virginia Geological Survey, vol. 1; by I. C. WHITE, State Geol. (Morgantown, West Va., 1899, 8°, 392 pp.)—In addition to the administrative report this volume contains a discussion of magnetic declination for the state with description of meridian monuments by R. U. GOODE. The State Geologist himself contributes a list of levels above tide and a particularly valuable report on the petroleum and natural gas of the state. This is treated both from theoretic and practical standpoints and will be found of great service to those engaged in a study of these products. It is to be hoped that the state will continue the survey and permit the publication of other valuable material which has been accumulated. L. V. P.

8. A new and interesting olivine-melilite-leucite rock.—The rock of one of two small volcanic cones discovered by E. Clerici at San Venazo in Umbria, about half way between Orvieto and Perugia, has been described by V. SABATINI in a note (dated September, 1898) in the Bolletino del Reale Comitato Geologico for 1898, as a leucitic melilitite with olivine. Olivine occurs as phenocrysts, and the groundmass is composed of melilite, leucite, black mica, and a little pyroxene, nephelite and magnetite, feldspars being absent. The melilites are zonally built, the interior being optically positive and the exterior negative. Sabatini proposes for this type the name Venanzite.

At the meeting of the Berlin Academy of Sciences held Feb. 9, 1899 (Sitzungsberichte, vii, p. 110, 1899), Prof. Rosenbusch read a paper on "Euktolite, a new member of the theralitic effusive magmas." This rock is identical with that of Sabatini, coming from the same locality, and his description is practically the same though more detailed, and with chromite and perofskite added to the list of component minerals. An analysis gave:

SiO 41.43, TiO<sub>2</sub> 0.29, Al<sub>2</sub>O 9.80, Fe<sub>2</sub>O<sub>3</sub> 3.28, FeO 5.15, MgO 13.40, CaO 16.62, Na<sub>2</sub>O 1.64, K<sub>2</sub>O 7.40, H<sub>2</sub>O 1.11 = 100.12. P<sub>2</sub>O<sub>3</sub> none. Sp. gr. = 2.758.

<sup>2</sup>He compares it with the madupite of Cross, leucities, and leucite and melilite basalts, all of which belong to his theralitic magmas. The name is derived from  $\epsilon i \kappa \tau \delta s$ , desired, since it is "a desired example for the validity of my representation of the intimate connection of the eruptive rocks throughout the world." Sabatini's name Venanzite antedates Euktolite by about five months and on the grounds of priority is unquestionably the one by which this interesting type should be known, especially since it is formed from the type locality, in accordance with modern usage in petrography, and does not involve the tacit acceptance of any theory, however generally recognized.

H. S. W.

9. Deuxième Mémoire sur les Algues Marines du Groenland ; by L. KOLDERUP ROSENVINGE. Meddelelser om Gronland, xx, pp. 1-125, pl. i and 25 figs., 8°. Copenhagen, 1898. Om Algenegetationen ved Grønlands Kyster; ditto, pp. 131-242.-The paper first named is an important supplement to the author's Groenlands Havalger published in 1893. The material studied included the collections made by N. Hartz, principally at Scoresby Sound during the expedition to East Greenland under Lieut. Ryder and those made by A. Jessen and C. Ostenfeld in West Greenland, besides a few smaller collections. Of the algæ of the eastern coast, which had been less thoroughly explored than the western, only 32 species had been previously enumerated, but in the present work the number is estimated at 82 including several new species. The number of species previously known on the west coast was 143, which number is now increased to 167 including in the enumeration the species reported by Kuckuck from Umanak collected by Vanhoffen. The Lithothamnia were revised by Foslie. Among the novelties are three new genera, Ceratocolax, Dermatocelis and Arthrochete, each represented by a single species of parasitic habit. The paper is well illustrated and the notes are full and suggestive. The second paper by Dr. Rosenvinge is a valuable contribution to our knowledge of the distribution of the marine floras of the North Atlantic, which gives details as to the temperature and other factors which affect the growth of marine plants and tables showing the relations of the Greenland flora to those of northern Europe and the Atlantic coast of North America. In spite of the remoteness and inclemency of the Greenland coast, thanks to the publications of Rosenvinge, Kjellman and other Scandinavian algologists, its marine flora is more accurately known than that of any other portion of the Atlantic coast of America. W. G. F.

10. Monographie des Caulerpes ; by Mme. A. WEBER-VAN Bosse, Ann. Jardin Bot. Buitenzorg, xv, pp. 243-401, pl. xxxxiv.-In a short introduction the author gives a summary of what is known regarding the cell structure with notes as to the probable fructification of the species of this large and peculiar genus, for, in spite of their abundance and wide distribution in all warm seas, no one has as yet succeeded in detecting with certainty their method of reproduction. The monograph is essentially a systematic study of the species for which the author is especially well qualified, since her excursions to the tropics have given her abundant opportunity for observing the Caulerpae in a living condition, while, on the other hand, she has been able to examine the dried specimens of practically all of the large algological herbaria. The subdivisions of the genus adopted are those of Prof. J. G. Agardh, but the number of species recognized by Mme. Weber is considerably smaller than in other works on the genus. In thus uniting the older described species the author, we think, has shown good judgment, and her excellent presentation of the subject gives a much better view of the genus

as a whole than has been possible to obtain hitherto. Especially in her treatment of the Thuyoideae and Claviferae is the author to be commended. One is at first struck by the very large number of species reduced to synonyms under such species as  $C_{\star}$ cupressoides and C. racemosa, which latter name replaces C. clavifera as generally used hitherto. But one who has had the opportunity of examining large sets of specimens can hardly fail to approve the specific limitations adopted by the author, for not only are the species themselves very variable but, also, one more than suspects that many of the species previously described owed their assumed characters to some accident of preparation. The arrangement of the present monograph seems to us to be the natural one and one which is likely to be generally adopted.

W. G. F.

11. De dispositione Delesseriearum; by Prof. J. G. AGARDH, pp. 239, 8°, Lund, 1898 .- This volume, which forms the third part of the third volume of the classic Species Genera et Ordines Algarum, of which the first volume appeared in 1848, is a rare illustration of continued scientific activity in a field in which the writer has been a master for more than sixty years. To American algologists it is of special interest, as it includes a revision of the species of Nitophyllum, Delesseria and related genera from our Pacific coast which were originally described in Agardh's Epicrisis and subsequent memoirs, to which are added Nitophyllum macroglossum, N. stenoglossum, N. marginatum, N. Farlowianum, Neuroglossum lobuliferum. The new genus Erythroglossum with five species includes Delesseria Woodii and D. Californica, and Apoglossum includes D. dicipiens, all three Californian species. The new genus Calloseris is founded on a single species, C. Halliae, from Florida. W. G. F.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. National Academy of Sciences.-The spring meeting of the National Academy was held in Washington from April 18 to 20. The following gentlemen were elected members : Charles E. Beecher of New Haven; George C. Comstock of Madison; Theo-dore W. Richards of Cambridge; Edgar F. Smith of Philadel-phia; Edmund B. Wilson of New York. The list of papers accepted for reading is as follows:

W. K. BROOKS and CASWELL GRAVE: Ophiura Brevispina.

A. HALL: The shadow of a planet.

A. AGASSIZ: Un the Tanner deep-sea tow net. On the diamond and gold mines of South Africa.

A. AGASSIZ and A. G. MAYER: On the Acalephs of the East Coast of the United States.

E. C. ANDREWS: On the limestones of Fiji. W. McM. WOODWORTH: On the Bololo of Fiji and Samoa.

CHAS. D. WALCOTT: Progress in surveying and protection of the U.S. Forest Reserves.

GIFFORD PINCHOT: The work of the Division of Forestry, Department of Agriculture.

H. S. PRITCHETT: The resulting differences between the astronomic and geodetic latitudes and longitudes in the triangulation along the Thirty-ninth Parallel.

A. GRAHAM BELL: On the development by selection of supernumerary mammæ in sheep. On kites with radial wings.

S. NEWCOMB: Remarks on the Work of the Nautical Almanac Office during the years 1877-98 in the field of Theoretical Astronomy. W. K. BROOKS and L. E. GRIFFIN: Exhibition of specimens of Nautilus pom-

W. K. BROOKS and L. E. GRIFFIN: Exhibition of specimens of Nautilus pompilius.

The third memoir of volume viii of the Memoirs of the Academy has recently been issued. The title of the paper is: General perturbations of Minerva (93), by Jupiter, including terms only of the first order with respect to the mass, together with a correction of the elements, by W. S. Eichelberger, Ph.D.

2. Annual Report of the Board of Regents of the Smithsonian Institution, to July, 1897; pp. xlvii, 686. Washington, 1898.— The Report of the U.S. Natural History Museum, under the direction of the Smithsonian Institution, for 1896, was noticed in the last number, and we have now issued the Smithsonian Report for 1897. The early portion of this is devoted to an account of administrative matters, by the Secretary, Professor S. P. Langley. This occupies some eighty pages. The remainder of the volume, or General Appendix, contains reprints of a well-selected series of papers on a very wide range of subjects; these include memoirs on astronomy, physics (X-rays, etc.), chemistry and so on through to archæology. The volume closes with an obituary notice of George Brown Goode by S. P. Langley, and one of Francis Amasa Walker by G. F. Hoar and C. D. Wright.

3. Harper's Scientific Series.—The recent additions to the series of Harper's scientific memoirs include Volume III, on Röntgen Rays, edited by Professor GEORGE F. BARKER of Philadelphia, and Volume IV, on the Modern Theory of Solution, edited by Dr. HARRY C. JONES of Johns Hopkins University. The first of these contains the original paper by Röntgen, and also others by Stokes and J. J. Thomson. Each of the papers is followed by a biographical sketch of the author, and the bibliography of the subject is added at the end. This subject is one of very great interest at the present time, and indeed this statement may also be made about Volume IV on the Theory of Solution. This latter contains papers by Pfeffer, Van 't Hoff, Arrhenius, and Raoult, with the usual useful editorial matter.

#### OBITUARY.

DR. GUSTAV WIEDEMANN, the distinguished physicist, for twenty-two years (1877-1899) editor of the Annalen der Physik und Chemie, died on March 23 at the age of seventy-three.

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## ΤΗΕ

## AMERICAN JOURNAL OF SCIENCE

## [FOURTH SERIES.]

## OTHNIEL CHARLES MARSH.

Among the leading men of science in America, Professor Marsh was unquestionably one of the best known, and had one of the strongest personalities. The world-wide reputation he enjoyed, however, is not altogether attributable to the particular department of research in which he stood without a peer, for, added to his attainments in Vertebrate Paleontology, he possessed an unusual number of mental qualifications in other lines, as well as marked personal characteristics which made him known and felt where his science could never reach. His fame will undoubtedly rest on his work among the Fossil Vertebrates. Nevertheless, his energy and attainments in other directions were sufficient to have made for him a permanent record.

The nearness of the perspective at the present time renders it difficult properly to individualize and accord the true rank to the many important discoveries Marsh has made. He brought forth in such rapid succession so many astonishing things that the unexpected became the rule. The science of Vertebrate Paleontology could not assimilate new material so fast, and it will be years before the true significance and bearing of much that he has done will be understood. The constant stream of vertebrate riches which, from 1868 to 1899, flowed into the Yale University Museum from the Rocky Mountain region had a similar bewildering effect on Marsh, for

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it was impossible for him to do more than seize on what appealed to him as the most salient. The work of the hour was to him of prime importance, whether it was for the determination of a new order of mammals or a new cusp on a tooth. Still, he seems to have had a just conception of relative values, for it will be found that he plucked the most luscious plums from the paleontological tree, and left chiefly the smaller or unripe and imperfect fruit untouched.

Another element in his success was seen in the improvement he made in the methods of collecting, preserving, and developing vertebrate fossils, so that even forms long known only from fragmentary remains were represented in his collections by almost complete specimens, presenting nearly the same degree of novelty shown in forms actually new.

In illustration of this, the Brontotheridæ, Ceratopsia, and the Mosasauria furnish excellent examples. Prout, in 1846. described, as *Palaeotherium*, the fragment of a lower jaw from the Miocene of Nebraska, but Marsh first showed the affinities and range of forms in the group, through his splendid restoration of Brontops and the description of a number of allied types from nearly perfect material. Cope, in 1875, figured some pieces of bone of unknown relationships, which long remained in the paleontological scrap-basket.\* Marsh, by his descriptions of the marvelous series of genera and species belonging to the Ceratopsia, demonstrated what these reptiles really were, and gave to science a nearly complete knowledge of one of the most bizarre monsters known. The first Mosasaur was obtained in Holland previous to 1785. Tt remained imperfectly known for nearly a century, when Marsh, by his contributions to its anatomy, made possible a clear understanding of its structure and affinities. In the same way it could be shown that to many old descriptions of genera and species based upon single teeth, he was enabled to add a knowledge of the remainder of the animal. Not only did he thus contribute the missing information in regard to many previously described forms, but he brought out a host of entirely new types, and made his science one of the most complete exponents of the doctrine of evolution.

\* Polyonax.

As a collector, Marsh was seen at his best, and the collections he amassed during his forty-five years and more of activity in this direction form a lasting monument to his perseverance and foresight. A person with means and inclination may be supposed to have the necessary qualities for accomplishing his aims, whether they are first editions, autographs, or fossils, but had Marsh possessed no further qualifications than these, the results of his collecting would fall far short of what he really attained. He not only had the means and the inclination, but entered every field of acquisition with the dominating ambition to obtain everything there was in it, and leave not a single scrap behind. Every avenue of approach was made use of, and cost was often a secondary consideration. The nine-tenths, when attained, were only an additional stimulus for securing the remaining one-tenth. Of course, this ideal of completeness was often impossible of accomplishment, and yet it served to bring to the Yale University Museum collections which are unique from their richness and extent.

In making an estimate of his character, it must not be forgotten that he developed wholly without the influence of family and home ties, which in most men profoundly mark their mature life. Self-reliance is probably the strongest trait fostered by the absence of immediate family connections. This, Marsh possessed to an extraordinary degree, and it naturally led to a self-centering of his life and ambitions. Out of it came, also, an absence of the complete exchange of confidence which normally exists between intimate friends. Even where perfect confidence existed, he seldom revealed more about any particular matter than seemed to him necessary or than the circumstances really demanded. As a friend, he was kind, loyal, and generous. As a patron of science, he has seldom been equaled. Honest work in any department appealed to him strongly, and he was ever ready with aid and counsel, even at the expense of a personal sacrifice. His disposition was a most happy one, and he was always keenly appreciative of the humorous and ludicrous and fond of relating amusing experiences and anecdotes. The sunny side of his

character was nearly always uppermost, and the consideration of subjects of the greatest gravity was enlivened by constant sparkles of wit from his exhaustless store.

He was normally restive under restraint, and met all opposition with power and fearlessness. Having practically created the modern science of Vertebrate Paleontology in America, he resented any encroachment upon the particular fields of research in which he was engaged. This attitude frequently developed feelings of hostility in other investigators, and often alienated him from co-workers in his department of science. Nevertheless, he labored faithfully for the truth as revealed in his work, and was ready to change opinions and published statements whenever facts seemed to warrant it.

His esthetic sense was highly developed, and could be seen in the artistic care he bestowed upon his publications, but more especially on his home. His grounds are a model of landscape gardening. He delighted in his collections of modern paintings, the cultivation of orchids, and above all in the subtleties of Japanese art.

The world was not slow to recognize his contributions to knowledge, for during his lifetime he received a large number of tangible evidences of distinguished consideration in the way of academic and scientific honors, medals, and membership in learned societies.

In 1886, he received the degree of Doctor of Laws from Harvard University, and in the same year the honorary degree of Doctor of Philosophy from the University of Heidelberg. He occupied the chair of Paleontology in Yale University from 1866 to the time of his death. He was Vertebrate Paleontologist to the United States Geological Survey, and Honorary Curator of Vertebrate Paleontology in the United States National Museum.

He was President of the American Association for the Advancement of Science in 1878, and of the National Academy of Sciences from 1883 to 1895. As a presiding officer in the National Academy, he exercised the same amount of care that he bestowed upon his private affairs, and was an active and efficient leader. In 1877, he was the recipient of the first Bigsby Medal awarded by the Geological Society of London, in recognition of his important labors on the Vertebrate Paleontology of the western territories of the United States. In 1898, the highly valued Cuvier Prize was given him by the French Academy, as one of the most able continuators of the science of which Cuvier had laid the foundations.

Prominent among the various societies of which he was a member may be mentioned :

The National Academy of Sciences: Institute of France; Royal Academy of Sciences, Brussels; Royal Bavarian Academy of Sciences, Munich; Royal Academy of Sciences, Bologna; Royal Danish Academy of Sciences, Copenhagen; Royal Irish Academy; Geological Society of London; Geological Society of Germany; American Philosophical Society; Academy of Natural Sciences, Philadelphia; Zoological Society of London; Société Impériale des Naturalistes, Moscow; Geological Society of America, etc., etc.

Few men have contributed more to THE AMERICAN JOURNAL OF SCIENCE than Professor Marsh. Nearly all his discoveries in science were first announced here, and it is the storehouse of most of his best work.

The subject of the present sketch was born near Lockport, New York, October 29, 1831. His parents were Caleb and Mary Peabody Marsh, formerly of Danvers (now Peabody), Massachusetts. His early education was obtained in the schools of Lockport and at the Wilson Collegiate Institute, Wilson, New York. A residence in a region rich in minerals and fossils is apt to attract the attention of a youth possessing healthy intelligence, and young Marsh soon shared his vacation time between the normal pursuits of shooting and fishing and the more unusual vocation of collecting minerals and fossils. By the time he was nineteen years old, he had thus acquired the taste for scientific subjects which was destined to grow and dominate the remainder of his life.

In 1851, he entered Phillips Academy at Andover, Massachusetts, and continued his studies there until graduation in 1856. He immediately entered the freshman class in Yale College, pursuing the regular classical course, and receiving the degree of B.A. in 1860. Graduate courses in the natural sciences were continued in the Sheffield Scientific School during the two years following (1861-62). The long summer vacations from 1851 to 1862 were occupied in collecting minerals and fossils from New York, New England, and Nova Scotia. To the latter region he made five trips during this interval, and obtained much valuable experience and scientific material. On his second visit (1855) he found some fossil vertebræ in the Coal Measures at South Joggins, representing a new and important vertebrate animal (*Eosaurus*). This discovery finally directed his studies into the channel which became his life-work. At this time, however, his interests were about equally divided between invertebrate paleontology and mineralogy, and it is worthy of note that his first scientific paper was published in THIS JOURNAL in 1861, under the title "The Gold of Nova Scotia."

The description of *Eosaurus* did not appear until 1862, seven years after its discovery. Even then it cannot be said that he had developed a strong liking for vertebrate paleontology. This closes the account of his student life in American schools.

The next three years were passed in study abroad, in the universities of Berlin, Heidelberg, and Breslau. He attended lectures and took special courses with H. Rose, G. Rose, Ehrenberg, Peters, Ræmer, Grube, and Gæppert. The vacations were occupied, as before, by geological excursions. He visited the most important localities in Europe, and obtained extensive collections. His official connection with Yale College began by his appointment, in 1866, to the chair of Professor of Paleontology. This title he held in high esteem, as it was the first established either in this country or elsewhere.

After attending the meeting of the American Association for the Advancement of Science at Chicago, in 1868, Marsh went as far west as Nebraska and Wyoming, along the route of the Union Pacific railroad, then just opened. This trip gave him a foretaste of the inexhaustible fossil riches of the Rocky Mountain regions, and thenceforth his energies were mainly devoted to their exploration. Scientific expeditions to the western country were undertakings of considerable magnitude in those early days. There was but one railroad in the United States across a region measuring fifteen hundred miles square. White settlements were sparse and remote. Most of the country was unmapped, and with the exception of a few transcontinental trails, almost the whole western half of the continent, save the regions bordering the Pacific, was a boundless expanse of unknown arid plains, mountains, and valleys. Added to these conditions were the indigenous tribes of war-loving Indians, hostile to the whites. Under such circumstances, travel was slow, difficult, and dangerous. It was necessary to have an escort of soldiers and guides, experienced in western life and Indian warfare.

The first Yale Scientific Expedition was organized and engineered by Marsh in 1870. The party consisted of thirteen persons besides the officers and men of the military detachments who escorted them from various military posts along the route.\* They explored the Pliocene deposits of Nebraska and the Miocene of northern Colorado, then crossing into Wyoming they made collections in the Eocene (Bridger Basin), and passing south discovered a new Eocene basin in Utah (Uinta Basin). At each of these places many important finds were made. The party next visited California, where minor collections were obtained from the Pliocene. Returning, they

\*Members of the Yale party were O. C. Marsh, C. T. Ballard, C. W. Betts, A. H. Ewing, G. B. Grinnell, J. W. Griswold, J. R. Nicholson, C. McC. Reeve, J. M. Russell, H. B. Sargent, J. W. Wadsworth, E. Whitney, Jr., and H. D. Ziegler. The escorts consisted of:---

From Fort McPherson, Nebroska.—Commanding officer, Gen. Eugene A. Carr. Lieuts. Bernard Reilly, Jr., and Earl D. Thomas, in command of escort, 5th Cavalry; Buffalo Bill and Major Frank North, guides; and two Pawnee Indian scouts ("Lahurasoc" and "Tuckatelous").

From Fort D. A. Russell, Wyoming.—Commanding officer, Gen John H. King. Capt. Robert H. Montgomery and Lieut James McB. Stembel, in command of escort, 5th Cavairy.

From Fort Bridger, Wyoming.—Commanding officer, Major R. S. LaMotte, Lieut. W. N. Wann, in command of escort, 13th Infantry: Mexican guide ("Joe Talemans").

From Fort Wallace, Kansas - Commanding officer, Gen. Henry C. Bankhead. Ed. Lane, guide; Lieut. Charles Braden, in command of rescue troop. spent some time exploring the Cretaceous beds of western Kansas, so rich in the remains of aquatic reptiles, and now famous for having furnished the first toothed birds and American toothless flying reptiles.

The second, third, and fourth Yale Scientific Expeditions (1871, 1872, 1873) were modeled after the first. New regions in the West were visited, and extensive series of remains of extinct animals were obtained. Coincident with these discoveries, Marsh published frequent scientific papers describing and illustrating the more important forms, and paleontological literature was enriched by the addition of more startling and wonderful types of animal life than had been hitherto known from the rest of the world.

Owing to Indian outbreaks and a general uneasiness in the West, no regular expedition was organized in 1875. Late in the fall, however, Marsh went to the Bad Lands of Nebraska and Dakota accompanied by an escort from Fort Laramie to the Red Cloud Agency. The consent of the Indians was deemed necessary to search for fossil bones in their country. A treaty was obtained with difficulty and then assistance was withheld. Nevertheless, with great hardship owing to extreme cold, the party succeeded in reaching the desired region, and made important discoveries, among which numerous remains of the gigantic Brontotheridæ are the most noteworthy.

It was at this time that he became aware of the frauds practiced upon the Indians by the agents of the Government, and the way the Government was in turn defrauded through their misrepresentations. He promised Red Cloud to bring the matter before the President for redress. This was done with signal success, resulting in the complete routing of the Indian Ring, and the downfall of the Secretary of the Interior as well as in his political death.

The rapid settlement and development of the West rendered it no longer necessary to fit out expensive expeditions, especially as many of the localities were easily accessible by railroad. Therefore, after 1876, local collectors and small parties were employed in continuing the work of collecting fossils so successfully begun by the Yale Scientific Expeditions. Nearly every season, however, Marsh visited the localities where work was being carried on, and some time each year was spent in reconnaissance for new fields of labor.

The right wing of the Peabody Museum was completed in 1875, the means having been furnished by Mr. George Peabody largely through the influence of his nephew, Professor Marsh. It was to his uncle, also, that Marsh was indebted for his educational advantages and for his private fortune. The old Yale Cabinet had long been outgrown. The rooms became so crowded that for years there was only space for a chalk line dividing the different departments. The collections which had been accumulating during so many previous years found a commodious home in the new museum, and work was resumed with great activity under more favorable conditions than heretofore. Huxley's visit in the following year was a further stimulus to higher work, as is clearly evinced in the celebrated Nashville address mentioned elsewhere.

The National Government had not altogether neglected its opportunities for scientific research in the West during this period, though the results in the way of substantial collections were far inferior to those Marsh had obtained. For some time previous to 1878, there were four separate surveys, two under the Engineer Department of the Army and two others, extensions of private expeditions, under the Department of the Interior. In the reorganization ordered by Congress in 1878, Marsh, as acting President of the National Academy of Sciences, was the chief instrument in effecting a consolidation and in defining the relations of the present United States Geological Survey with the general Government and with the United States National Museum. The wisdom of this change was at once apparent, and the Survey is now often considered one of the most economical, best managed, and productive departments of the Government.

After repeated solicitation and with promises of material aid in the way of publication and collections, Marsh, in 1882, accepted the appointment of Vertebrate Paleontologist to the United States Geological Survey. This position he held to the time of his death, although the field work for the survey was terminated in 1892. His connection with the Survey gave him increased facilities for publication and for prosecuting explorations in the West. He successively projected the publication of a number of large monographs on various groups of vertebrate fossils. It is a great misfortune that but two of these were ever finished by the author. The monograph of the Odontornithes appeared in 1880, and that of the Dinocerata in The others were left in various stages of incomplete-1885 ness at the time of his death. The proposed volumes treated of the Sauropoda, the Brontotheridæ, the Stegosauria, Theropoda, Ornithopoda, Mesozoic Mammals, and the Ceratopsia. Most of the investigations had been completed, a large part of the plates and figures engraved, and preliminary descriptions published, but the philosophical and phylogenetic problems are largely untouched. The loss to science is greatest in the volumes relating to Reptiles, especially the Dinosauria, for in this subject Marsh stood as the sole possessor of an acute and comprehensive knowledge of one of the most wonderful and difficult groups of vertebrates known. He planned his life-work on the basis that immortality is here and not in the hereafter. It seemed difficult for him to realize the limitations of human existence and worldly accomplishment.

In the closing years of his life he had two ruling ambitions, first, to see the main building of the Museum erected, and, second, the completion of his monographs. The accomplishment of the first is imperative and would permit of the proper care and display of the priceless treasures he has accumulated. The attainment of the second would cancel his obligations to science. Neither was realized.

As one of the trustees of the Peabody Museum and as Curator of the Geological Collections, Marsh performed his chief duties in connection with Yale University. The final transfer to the University, of all the collections he had accumulated, was made January 1st, 1898, and soon after the gift was accepted by the Corporation. These collections are so extensive as to merit particular attention, especially since they represent the most valuable part of the work of a lifetime, and form the chief monument of one of Yale's most noted men. As expressed in the deed of gift, the collections comprise : 1. The Collection of Vertebrate Fossils. This is the most important and valuable of all. It is very extensive and contains a large number of type specimens, many of them unique, and is widely known from the descriptions already published. In extinct Mammals, Birds, and Reptiles, of North America, this series stands preëminent. The collection was pronounced by Huxley, who examined it with care in 1876, to be surpassed by no other in the world; and Darwin, in 1878, expressed a strong desire to visit America for the sole purpose of seeing it. Since then it has been more than doubled in size and value, and still holds first rank. The bulk of this collection was secured in western explorations, which were extended over a period of nearly thirty years.

2. The Collection of Fossil Footprints. These specimens are mainly from the Connecticut Valley, and thus have a special local interest.

3. The Collection of Invertebrate Fossils. This includes a large amount of interesting material from many formations and localities, both in this country and in Europe. Among the series of specimens especially valuable may be mentioned several thousand from the famous Mazon Creek locality in Illinois; a very extensive collection of Crinoids from Crawfordsville, in Indiana; the largest collection of nearly entire Trilobites yet discovered; and one of the rarest series of Silurian Sponges known, including important type specimens.

4. The Collection of Recent Osteology. This is believed to be one of the most complete collections in this country for purposes of study. Special efforts have been made for many years to secure the skeletons of rare existing vertebrates from every part of the world, particularly of Mammals, Birds, and Reptiles. The collection is especially rich in Anthropoid Apes.

5. The Collection of American Archeology and Ethnology. This collection is replete in Central American antiquities, comprising several thousand, many of them unique. Among others is the famous deZeltner collection from the same region, containing a number of gold ornaments. The specimens from Mexico are also of great interest, and the series is a representative one. It includes the well-known Skilton collection.

6. The Collection of Minerals. This is a limited collection, but contains many valuable specimens, among them probably

the most interesting series known of Nova-Scotian Zeolites. These were mainly collected by Marsh, before he was graduated at Yale, during six expeditions to Nova Scotia.

Besides the six main collections named, there are several others of less value, which include fossil plants, casts of fossils, geological specimens, and recent zoological material.

To these should be added the results of his last work in endeavoring to increase the scope of the material in the Peabody Museum. For many years it was his desire to secure a collection of fossil Cycads, and when the opportunity offered, he embraced it with characteristic vigor, so that within the last year and a half the Museum has received an amount of material which in importance and quantity is second to none.

From their extensive and varied nature, these collections thus presented to the University will long afford abundant material for original investigations, and will ever attract to New Haven specialists in Paleontology and Archeology.

Professor Marsh's life was remarkably free from the petty annoyances of poor health which so often interfere with human comfort and ambitions. In the midst of his scientific work and while making plans for the growth of the Museum, he was suddenly overtaken by the malady which resulted in his death. He died of pneumonia, on March 18th, 1899, in his sixty-eighth year, after an illness of about a week. His work as an investigator in natural science, his wonderful scientific collections, and his munificence to Yale, are his legacies to the higher education of mankind.

Although Marsh was an ardent collector in Archeology, he published very little on this subject, and his paper (1866) on an Ancient Sepulchral Mound near Newark, Ohio, is practically the only one. His three mineralogical papers, published between 1861 and 1867, show the results of considerable labor and careful investigation. They treat of the Gold of Nova Scotia, a Zeolite mineral from the same region, and a catalogue of the mineral localities of the maritime provinces of Canada.

In the field of Invertebrate Paleontology, he likewise was an indefatigable accumulator of material, though after 1869 he published nothing in this department. Two papers presented some Annelids considered as new, from the Jurassic of Germany. Another showed the origin of the double lobe-lines in *Ceratites*. His papers on American invertebrates comprised a description of a new genus of Fossil Sponge (*Brachiospongia*), a new form of Crustacean Trail from the Potsdam Sandstone, and a note on color markings in *Endoceras*. He also showed that *Palæotrochis* and *Lignilites* were not of organic origin, though the contrary had been previously supposed.

In the domain of Geology, his chief interests lay in the formations from which he secured important series of fossil vertebrates. Probably his greatest geological discovery was the Uinta Basin, an Eocene deposit of the eastern Uinta Mountains. It was first visited in 1870. Having studied most of the Tertiary lake basins in the Rocky Mountain region, he gave, in 1875, a synopsis of their geological features. As a natural result of studying Geology in Germany, he was much impressed with the methods of marking the separate horizons by means of some characteristic fossil. He believed the vertebrates were the most sensitive time-markers, and therefore endeavored to determine and limit geological horizons wholly by fossil vertebrate remains. The inherent fault of this system is that the vertebrates are not always the most highly differentiated and specialized types in any given fauna, and it is these qualities alone that can be safely employed in organic chronometry. This method is usually of great value in freshwater deposits rich in vertebrate remains, but it can be seldom used to advantage in marine sediments or in formations containing a scanty vertebrate fauna. Thus, while the name Equus Beds is very appropriate for a horizon in the Pliocene, on account of the abundance of remains of fossil horses, the same cannot be said of the term Eosaurus Beds as an equivalent of the entire series of the Coal Measures, especially as but two vertebræ of this animal have ever been discovered. Geological facts will be found scattered through many of his publications dealing principally with fossil vertebrates. One of the latest problems to interest him was the age of the series of variegated clavs extending from Martha's Vineyard south along the Atlantic coast into Maryland. His investigations led him to refer them to the Jurassic, a formation which had been considered as absent in eastern North America.

There yet remains for consideration the real work of his life,—his publications on the Fossil Vertebrates, and it is at once evident, from a glance at the bibliography, that his chief researches were upon the Reptiles, Birds, and Mammals. There are three papers on Fossil Fishes, containing notices of several new forms, but no real research in this class was ever undertaken by him. The Amphibians also claimed but little attention, and his observations on the metamorphosis of the recent *Siredon* into *Amblystoma*, and two brief notices of amphibian footprints in the Devonian and Carboniferous, comprise the whole.

It is with extreme hesitation and a sense of inadequacy that the writer ventures to review, even in the briefest and most superficial manner, the work which undoubtedly constitutes the literary essence of his life-work. Future investigators alone can critically estimate the great mass of facts which Marsh brought out and which he wove into the departments of fossil Reptiles, Birds, and Mammals.

His most comprehensive work, and in many ways the most masterly, is the address delivered before the American Association for the Advancement of Science, at Nashville, in 1877. In this paper, entitled the "Introduction and Succession of Vertebrate Life in America," he traced the introduction of the various types of vertebrate life then known in America, beginning with the lowest fishes and ending with man. The amount of knowledge on the lower classes of vertebrates, including the reptiles, was then too meager to enable him to give more than occasional hints as to their phylogeny. But his handling of the Mammalia showed the clearest insight into the development and affinities of many of the important types, and marked him as a true philosopher.

A glance at the modern text-books of Geology and Paleontology reveals how much America has done for the fossil vertebrates in the three classes of Reptiles, Birds, and Mammals. It will also show that Marsh contributed more than any other investigator toward the prominence now accorded to the American forms.

## Othniel Charles Marsh.

His work on the Reptilia is not equally divided among the various orders, for the Dinosauria claimed his attention above all others. To this group he lent his best efforts, and he compassed it so thoroughly as to be its sole master. It seems only necessary in this place to notice the complete restorations he made of some of these remarkable animals. In this list are included Anchisaurus, Brontosaurus, Laosaurus, Ceratosaurus, Camptosaurus, Stegosaurus, Triceratops, and Claosaurus. It must be remembered that nearly all these animals were of gigantic stature, some of them the largest land animals yet known, and also that each restoration represents a number of separate investigations on the structure of the skull, the limbs, the vertebræ, the pelvis, etc. In most cases, only by this means was it possible to bring together gradually, part by part, until the sum of the knowledge warranted a complete representation of the skeleton. The material of many of the genera he described is still in these various stages of progress, awaiting new additions of portions yet unknown in order to form a finished conception of the entire animal. His extensive report on the Dinosaurs of North America, published in 1896, gave a synopsis of what he had accomplished up to that time, but as remarked elsewhere their philosophical treatment he had reserved for his final monographs.

Probably, among the Reptilia, next in importance to his work on the Dinosauria is that on the Mosasaurs. In this he first announced the discovery of the dermal armor, the position of the quadrate, the finding of the stapes, the columella, the hyoid, the sclerotic plates, the quadrato-parietal arch, the malar arch, the transverse bone, the pterygoids, the pterotic bone, the sternum, the anterior limbs, the posterior limbs, the length of the neck, and details of the pelvic region. Thus he contributed a knowledge of some of the most essential characters of the skeleton in this group. In other groups of aquatic reptiles, he also brought out new genera and types of structure. Prominent among these may be mentioned Baptanodon, a toothless Ichthyosaurian. Marsh was the first to describe the remains of fossil serpents in the western Tertiary deposits, and likewise the first to discover the remains of flying reptiles in America. The latter were of unusually large size and remarkable for the absence of teeth.

The acquisition of a unique specimen of Pterodactyl from the lithographic slates of Bavaria enabled him to supply the long sought information regarding the wing and caudal membranes. Notices of a number of new species of fossil Crocodiles, Lizards, and Turtles, complete this survey of his work on the Reptilia.

Practically, most of the present knowledge of extinct birdlife in America is contained in Marsh's publications, which include descriptions of numerous species, ranging from the Jurassic to the Post-Pliocene. Unquestionably, the one discovery which is always foremost in men's minds in a consideration of his work is the determination of an extinct order of birds possessed with teeth. The study of the Dinosaurs and Toothed Birds showed that one by one characters considered as avian were likewise present in reptiles, and that many reptilian characters were present in these primitive birds; so that at the end there did not seem much else besides feathers to distinguish them. Marsh's investigation of fossil birds led to the publication, in 1880, of his first monograph, "Odontornithes: a Monograph on the Extinct Toothed Birds of North America." In this volume, he carefully figured and described all the known types, and presented complete restorations of the two leading genera, Hesperornis and Ichthyornis. He concluded that birds most nearly resemble some of the small Dinosaurs from the American Jurassic, and that both classes originated at least as far back as the Trias or late Paleozoic, in some sauropsid type.

A discovery which rivaled that of the Toothed Birds, although not so wholly his, was the genealogy of the Horse. Huxley and Kovalevski traced the equine branch through the Pliocene to the Upper Miocene in Europe, but the true and remote ancestry remained unsolved until the American types were described by Marsh. He showed that a primitive and diminutive polydactyl horse existed in the Lower Eocene, and that from this type, by gradual and progressive change through successive horizons of the Eocene, Miocene and Pliocene, there had been evolved all the intermediate stages leading to the modern horse.

Next in importance and interest should be noticed the series of papers culminating in the monograph of the Dinocerata, issued in 1886 by the United States Geological Survey. His work in other groups of mammals is scattered through a large number of separate papers, and contributions were made to every known order. The Tillodontia comprise one of the most remarkable of the types. Among others are the first remains of fossil Primates, Cheiroptera, and Marsupialia, known from North America. The Brontotheridæ and Coryphodontia received considerable attention. A monograph had been begun on the former, and restorations of a typical genus of each were published.

One general conclusion of much significance was the outcome of his researches on the Mammals. It was that the Tertiary genera possessed very small brains. As a single example, *Dinoceras* may be taken. This animal was but little inferior to the elephant in bulk, but its brain capacity was not more than one-eighth that of existing rhinoceroses.

The first Mesozoic Mammal in America was described by Emmons, in 1857, from the Triassic of North Carolina. Marsh, by his extensive discoveries, was enabled to fill up the gaps to the Tertiary with many genera and species from the western Jurassic and Cretaceous. Probably nine-tenths of all the Mesozoic Mammals known in the world were described by him, and while these remains are of great interest, yet from their fragmentary condition they are not of the highest scientific value, because little is known beyond the jaws and a few limb bones.

In closing the outline of the discoveries made by this investigator, one cannot help being impressed with their signal brilliancy, their great number, and especially by their unique importance in the field of organic evolution. Were all other evidence lost or wanting, the law of evolution would still have a firm foundation in incontrovertible fact. The study of variation and embryology in recent animals gives hints as to the truth, but Paleontology alone can give the facts of descent.

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The Value of Type Specimens and Importance of their Preservation. *Ibid.*, pp. 401-405.

The Origin of Mammals. Ibid., pp. 406-409.

- The Comparative Value of Different Kinds of Fossils in Determining Geological Age. Abstract: *Ibid.*, pp. 483-486.
- On the Families of Sauropodous *Dinosauria*. Abstract: *Ibid.*, pp. 487-488.

1899 Footprints of Jurassic Dinosaurs. *Ibid.*, vol. 7, pp. 227-232, pl. v. Note on a Bridger Eocene Carnivore. *Ibid.*, p. 397.

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# ART. XLVI.—The Camden Chert of Tennessee and its Lower Oriskany Fauna; by JAMES M. SAFFORD and CHARLES SCHUCHERT.\*

# Part I. The Camden Chert. By JAMES M. SAFFORD, State Geologist.

In March, 1855, the writer discovered in Benton County, Tennessee, at several points, excellent outcrops of Lower Helderberg shales and limestones, very rich in fossils. The discovery was important, since it settled the question as to the presence of the Lower Helderberg, as a distinct formation, in Tennessee, west of the meridian of Nashville. In subsequent years, this discovery also led to a recognition of the chert now referred to as Oriskany, which I have designated the Camden chert for the reason that at Camden, the county-seat of Benton, is seen one of its best exposures.

One of the localities discovered in Benton County was a bluff on Big Sandy River, about five miles from its month, at a point then in Henry County, and known as the old William's Mill Site. This locality is referred to in "Geology of Tennessee," 1869. As stated on page 325 of that book, there are here exposed about 50 feet of bluish limestone, mostly shaly. Above this and running back on a slope from the precipitous portion of the exposure, "are loose, angular, flinty masses, containing the fossils of the rocks below, and derived from cherty layers not seen." The fossils in the chert were not numerous nor in good condition, but what was seen of them led, at the time, to the conclusion stated.

In 1884, I recognized the chert at Camden as a distinct formation. I had, in passing through the country, seen this horizon and had referred it without special examination to the "Silicious Group" (Lowest of Subcarboniferous), outcrops of which, very like the chert of Camden, are seen at many points in Benton and counties north and south of it. In my excursion of 1884, however, I stopped for some time at Camden to study the formations. The fossils in the chert arrested my attention, and reminded me of those in the flints seen at William's Mill in 1855. But at Camden, the chert was in comparatively great force, at least 60 feet of it being exposed. At first, I was inclined to consider the chert a division of the Lower Helderberg, but subsequent studies of the fossils at home forced me to the conviction that, as a group, they must

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be Oriskany. The fact that the formation was one of chert also pointed to this.

Afterwards, in 1885, 1886, and 1887, I visited localities where I thought the Camden might outcrop. One of these is Big Sandy Station, in Benton, on the Memphis branch of the Louisville & Nashville Railroad, and near the point where the road crosses Big Sandy River. Here I found the chert well developed and abounding in fossils. The outcrops are as extensive and as good as at Camden. For several miles south of Big Sandy, the chert appears on the hillsides as loose angular gravel.

Five miles south, on the Lower Camden road, Lower Helderberg limestones are seen cropping out from beneath Camden chert, with Tertiary beds also overlapping all in unconformable contact.

In Henry County the Camden chert outcrops in considerable areas, west and south of the William's Mill locality. It is seen in limited thickness above the Lower Helderberg in Decatur County, and in the same relation, cast of the Tennessee River, in Stewart County. In the latter locality, it outcrops in the bluff on the Cumberland River below Cumberland City. The greatest development of it, however, is on the west side of the Tennessee River, in a strip of country lying in Henry, Benton, and Decatur Counties.

In 1897, I called the attention of Mr. Schuchert to the Camden chert, at the same time trusting he might be able to visit the Camden locality. This he did, collecting a series of fossils, which he studied, kindly giving me the results. I am under special obligation to him for this visit.

#### Part II. The Camden Lower Oriskany.

#### By CHARLES SCHUCHERT.

In the spring of 1897, the writer collected for the U.S. National Museum Lower Helderberg fossils in western Tennessee, and while in Nashville, Professor Safford also directed his attention to a lot of Camden chert organisms. Since no strata of Oriskany age had been recorded in Tennessee, the importance of determining the equivalency of the Camden chert with other regions made it desirable to know more of its fauna, and with that object in view, a collection was made at Camden.

The fossils of the Camden chert are, as a rule, natural casts of both the interior and exterior of the organism, and preserve the fined markings in detail. This fauna is closely related to that described by Meek and Worthen\* from the "Clear Creek

\* Geol. Surv., III, vols. i, ii, and iii.

Limestone" of southern Illinois, Alexander, Jackson, and Union Counties. From this region are known but 11 species, and 8 of these are also found in Tennessee. They are Anoplia nucleata, Anoplotheca flabellites, Eatonia peculiaris, Spirifer worthenanus, S. hemicyclus, Megalanteris condoni, Amphigenia curta and Strophostylus cancellatus.

The "Clear Creek limestone" of Illinois is intimately connected with the Lower Helderberg below, and is not less than 200 feet thick, being followed by a "quartzose sandstone" from 40 to 60 feet in thickness. The latter is probably equivalent to the Upper, or typical, Oriskany of New York, and does not appear to be present in western Tennessee. From Professor Safford's description of the Camden chert, it is evident that the Lower Oriskany thins rapidly southward. In Tennessee, it is about 60 feet in thickness, while it is not less than 200 feet thick in Illinois exclusive of the Upper Oriskany, which is entirely absent in the former state.

The "Camden chert" fauna contains 32 species, and 6 of these are restricted to southern Illinois and western Tennessee. Of the entire fauna, 24 species are found either in the Lower Helderberg or in the Lower Oriskany of other regions, and 20 occur in the Upper Oriskany or Corniferous. After removing the 13 species common to both the Lower and Upper Oriskany, and the two restricted forms, 17 remain. Of these 10 occur either in Lower Helderberg of Lower Oriskany rocks of other regions, while 6 are found in higher beds. This evidence, therefore, indicates clearly a Lower Oriskany age for the "Camden chert" of Tennessee and the "Clear Creek limestone" of Illinois, which indication is the more marked because of the absence here of such characteristic Upper Oriskany species as *Hipparionyx proximus, Chonostrophia complanata, Spirifer arenosus, Rensselaria ovoides, Meristella lata, Camarotechia pleiopleura, C. barrandei*, or *C. speciosus*.

Lower Oriskany fauna of the Camden Chert of Camden, Benton County, Tennessee.

	In Lower Oriskany elsewhere.	In Upper Oriskany elsewhere.
Zaphrentis rœmeri Hall ?	L. H.*	
Pholidops terminalis Hall	×	×
Hipparionyx proximus Vanuxem? A very		
small specimen if this species	×	×
Chonetes mucronatus Hall?		$\times$
" melonica Billings	×	×
Chonostrophia reversa (Whitfield)		U. H.

\* L. H. = Lower Helderberg; U. H. = Upper Helderberg. This list is based on the collection in the U. S. National Museum.

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	In Lower Oriskany elsewhere.	In Upper Oriskany elsewhere.
Stropheodonta (Lepstrophia) perplana (Con-		0150 11 11 01 01
rad)	×	U. H.
Orthothetes woolworthanus Hall	×	
Anoplia nucleata Hall	×	×
Cyrtina affinis Billings	×	×
Metaplasia pyxidata Hall	×	×
Spirifer hemicyclus Meek and Worthen	×	
" tribulis Hall	×	×
" worthenanus Schuchert	×	
Anoplotheca flabellites (Conrad)	×	$\times$
Meristella lævis (Vanuxem)	×	
" sp. undet.		
Camarotechia tethys (Billings) ?		U. H.
Atrypa reticularis Linne	×	$\times$
Eatonia pecularis (Conrad)	×	$\times$
Amphigenia curta Meek and Worthen ?	×	
Rensselæria ovoides (Eaton)?	×	$\times$
Megalanteris condoni (McChesney)	×	
Tentaculites acula Hall	×	$\times$
Avicula cfr. obscura Hall	L. H.	
Actinopteria cfr. textilis Hall	×	
Acrocoulia magnifica (Hall) ?		$\times$
Acrocoulia (Orthonychia) tortuosa (Hall)?	×	$\sim$
Diaphorostoma turbinata (Hall)		U. <b>H</b> .
Strophostylus (?) cancellatus Meek and		
Worthen	×	
Phacops cristata Hall		×
Ostracoda.		
and the second se		
Total 32 species	24	20

# ART. XLVII.—Recent discovery of rocks of the age of the Trenton formation at Akpatok Island, Ungava Bay, Ungava; by J. F. WHITEAVES.

WHILE accompanying the Hudson Bay expedition despatched by the Canadian government in 1897, in the sealing steamer "Diana," Dr. R. Bell, of the Geological Survey of Canada, spent the 13th of September on Akpatok Island, on his way from Ashe Inlet to Fort Chimo. In a preliminary report on his explorations for that year,\* Dr. Bell says: "The portion of the island which I saw (from the northern end to the middle of the east side) consists of unaltered gray limestone in horizontal beds, and it presents a perpendicular wall 400 or 500 feet high all along." "This sea-wall is clean-cut and the beds appear thick and solid, but wherever their edges have been long exposed to the weather, or in the hill-sides and ravines of the interior, they split up into thinner layers." "Some fragments observed in one place had the appearance of lithographic stone." "I was enabled to land opposite the place where the Diana anchored, as already mentioned, about the middle of the eastern side, and I improved the opportunity to collect fossils, which, however, were not abundant." "Those obtained indicate the Hudson River formation."

When this last sentence was written, the specimens that it refers to had not been unpacked. Since the publication of the Report from which it and the four preceding sentences are quoted (in May, 1898), these fossils have been examined by the writer, and it at once became obvious, first, that they indicate a little lower geological horizon than the Hudson River forma-tion, viz., that of the Trenton limestone; and, secondly, that they are remarkably similar to the fossils of the Trenton formation of the Red River valley in Manitoba. The collection consists of fifteen species, but two of these are imperfect casts of the interior of shells of gasteropoda, that can only be determined generically. Of the thirteen that remain eleven had previously been found in the Manitoba Trenton, and nine are species that are common at East Selkirk and Lower Fort Garry. The two fossils of which by far the most specimens were collected are Streptelasma robustum and Cyrtoceras Manitobense. The former is a rather large rugose coral, the types of which are from the Red River valley in Manitoba.

The following is a list of the species represented in the collection, as far as they can be determined.

\* Summary Report of the Geological Survey of Canada for 1897, page 82.

Whiteaves—Trenton rocks at Ungava.

LIST OF FOSSILS FROM THE TRENTON FORMATION AT AKPATOK ISLAND, COLLECTED BY DR. BELL IN 1897.

#### RECEPTACULITIDÆ.

Receptaculites Oweni Hall.

A very small and worn but fairly characteristic fragment.

## ZOANTHARIA.

Streptelasma robustum Whiteaves. About thirty specimens, of all sizes.

## Calapæcia Canadensis Billings. One specimen.

#### BRACHIOPODA.

Rafinesquina lata Whiteaves. One ventral valve.

Leptæna unicostata Meek and Worthen.

A tolerably well preserved ventral valve that is apparently referable to this species.

Plectambonites sericea (Sowerby).

A few specimens.

#### Orthis tricenaria Conrad.

An unusually large ventral valve.

Orthis (Dinorthis) Meedsi, var. arctica Schuchert.

Three imperfect and badly preserved specimens which Mr. Schuchert thinks look very much like Baffin Land specimens that he is describing under this name.

#### Orthis (Hebertella) bellarugosa Conrad.

One good specimen that has been identified with this species by Mr. Schuchert.

#### Orthis (Dalmanella) testudinaria Dalman.

A few imperfect specimens.

#### Platystrophia biforata (Schlotheim).

Two imperfect ventral valves.

? Rhynchotrema inæquivalvis (Castelneau). An imperfect ventral valve, with the cardinal area not visible.

#### GASTEROPODA.

Trochonema or Pleurotomaria. (Species indeterminable.)

A cast of the interior of the last volution and last but one.

Hormotoma. (Species indeterminable, but apparently like H. Salteri Ulrich.)

A cast of the interior of three of the volutions.

## CEPHALOPODA.

#### Cyrtoceras Manitobense Whiteaves.

About thirty well preserved but much worn fragments, from less than an inch to nearly two inches in length.

Ottawa, March 23d, 1899.

ART. XLVIII.—Studies in the Cyperaceæ; by THEO. HOLM. X. Fimbristylis Vahl; an anatomical treatise of North American species. With fourteen figures in text, drawn from nature by the author.

THAT purely floral characters are insufficient for the establishment of genera has been proved by several botanists in recent years. This is especially the case with large orders, where a number of species are to be classified so as to demonstrate, at least, a supposed relationship. It is not uncommon that herbalists content themselves by studying only the floral structure and matching the details with some old illustration or analytical key; but there is, however, more than that to be considered and looked upon, as affinity and relationship. The establishment of natural orders is, of course, a progress, but, to say the least, the genera themselves are often so badly understood and so arranged, that we obtain no more knowledge of the real affinities than if we had followed the system of Linnæus: Monandria, Diandria and so on. It is very common to see species arranged in genera widely apart, on account of the stamens and stigmata being different in number, while the plants otherwise show the same habits and internal structure. Our genus *Fimbristylis* furnishes a good illustration. Merely because some species have two or three stigmata, this genus has been divided into Dichelostylis and Trichelostylis; and the fact that the base of the style is persistent in some species, but only for some time, has caused the separation of the genera Isolepis and Oncostylis.\* Furthermore these genera have been considered as subgenera of *Scirpus* or even as close allies of *Heleocharis*, a consideration, however, that cannot possibly have been based upon observations in the field. But to Bentham and Asa Gray such characters were of less importance, and these authors were liberal enough to include a number of species as true Fimbristyles, even if the floral characters did not come exactly within the scope of the original diagnosis or conception of the genus as understood by Vahl. Finally the anatomical study of a number of genera of the Cyperaceae has shown us that certain analogies exist which must be considered as valuable to the study of mutual affinities, promulgated by Schwendener, Palla<sup>+</sup> and Rikli.

<sup>\*</sup> It was Martius (Flor. Brasil.) who substituted the generic name Oncostylis for Bulbostylis, which appears in the Conspectus generum, because DeCandolle had already used Bulbostylis to designate a genus of Composite.

<sup>†</sup> Palla Ed. Zur Kenntniss der Gattung "Scirpus." (Engler's botan. Jahrbücher, vol. x, Leipzig, 1889, p. 293.)

AM. JOUR. Sci.—FOURTH SERIES, VOL. VII, No. 42.—JUNE, 1899.

Considering the genus Fimbristylis in North America not only "sensu strictiori," but including the species which Torrey reterred to Isolepis: stenophylla, ciliatifolia, Warei and capillaris R. et S., we cannot avoid noticing that the general habit of these plants, both annuals and perennials, is very much the same. A dense cespitose growth is characteristic of most of our species; the leaves are generally narrow with short sheaths, and the flowers are arranged in true spikes, either borne on long peduncles constituting open cymes, or sessile in small heads. While a pubescence is rarely observed in Cyperacea, it is not uncommon in Fimbristylis, of which several species have the leaves, stems, involucres and scales clothed with short hairs. In examining the inflorescence, the spikes are mostly, as stated above, arranged in open cymes, where the terminal spike is almost sessile and overtopped by the lateral ones. In F. castanea and F. thermalis several lateral spikes are borne on long peduncles, but with no further ramifications, representing respectively a di- or pleio-chasinm. A similarly constructed cyme is, also, characteristic of F. laxa in plants growing in the vicinity of Brookland, D. C.; in specimens from Eustis, subtropical Florida, the lateral inflores cences are, on the other hand, decompound, thus agreeing with F. spadicea. The pleiochasium in F. puberula is either simple or decompound; in the first case the spikes are considerably larger than in the last, where the spikes consequently are more numerous. The most decompound inflorescence is, however, to be found in F. autumnalis, where the secondary branches are pleiochasia, the tertiary, on the contrary, passing over into monochasia of only two spikes, a terminal and a lateral. While in F. capillaris the inflorescence is typically a pleiochasium, it is not unusual to meet with specimens where the flowers are reduced to a single spike, at the base of which a long involucral bract is often noticeable, but without supporting any lateral branch. Similar empty involucral leaves, but reduced to scalelike, long-pointed bracts, occur also at the bases of several of the spikes, indicating the place of non-developed inflorescential branches. In species with sessile spikes, F. Warei and F. stenophylla, the composition of the inflorescence becomes more indistinct, since all the peduncles are very short and the characteristic clado-prophyllon entirely suppressed, a fact that is known also from other genera of *Cyperace* with similarly aggregated spikes : species of Cyperus, Dichromena, Scirpus, *Carex* and others. But where a clado-prophyllon is developed, this is readily noticed at the very base of each lateral peduncle as a tubular sheath, more or less puberulent in our species of Fimbristylis. It varies somewhat in shape, being compressed in F. autumnalis and its more southern ally F. complanata.

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or bicarinate in F. castanea and F. spadicea, or it is cylindric as in the other species; the apex is prolonged into two subulate teeth in F. laxa and F. castanea, but merely slightly oblique in the others. While the inflorescence of Fimbristulis does not show any remarkable deviation from that of other Cuperacea, we have observed in the disposition of the leaves a very peculiar exception from the ordinary rule in this order, at least in some species. As invariably quoted in botanical manuals, the tristichous leaf-arrangement is the characteristic one of the Cyperaceae, while on the contrary the distichous that of the Gramineae. It would hardly be natural to suppose that any such rule should be stable for either of these orders, since exceptions are known if not from the leaves then at least from the arrangement of the spikelets and the inflorescential branches. We might merely call attention to the panicles of a number of Gramineæ, of which the branches are not distichous: besides that the spikelets are sometimes spirally arranged, as for instance in species of Eragrostis. In the Cyperacea the distichous arrangement of the flowers with their bracts is well known as the very characteristic of Cyperus, Dulichium, partly also of Scleria and Dichromena. But the arrangement of the stem-leaves has, so far, usually been described as tristichous in the Cyperaceæ, in spite of the fact that Kunth, in his diagnosis of F. autumnalis, characterized the leaves as "distichis," a statement which is absolutely correct. The leaves of this species have laterally compressed sheaths, which soon become split, and the blades are furthermore held in a very peculiar position: with the one margin turned towards. the axis or the flower-bearing stem. Although the leaf-blades are not isolateral, they invariably show this position, a fact that we have never noticed before in any of our American species with corresponding anatomical structure excepting in F. complanata. The distichous arrangement of the leaves is, however, also to be seen in F. castanea and F. spadicea, but the leaf-blades are not turned to the side in these species; they occupy the usual position as dorsiventral leaves. Considered from a morphological view-point, it seems strange that such disposition of leaves should be found in a genus like Fimbristylis, in which all the other foliar organs, involucral-leaves and floral bracts are arranged in spirals; it would seem more natural to a genus like Cyperus or Dulichium with the distichous flowers. And by examining the internal structure of such leaves, it seems still more surprising that we find a number of analogies rather than important variations. Furthermore when we compare our North American species with each other, it will be seen from the following pages, that even if they inhabit localities differing greatly in climate and soil, their internal

structure does not seem to be influenced to such an extent as to render it impossible to detect several and very gradual tran-The modern, but often too superficial and hasty sitions. classification of plants as Xero- and Hydro-phytes, is not by any means applicable to our genus, at least not to its North American representatives. If such types of plants, Xero- and Hydro-phytes, really exist, it must be proved not by observations in the field alone, but by a very close study of their structural peculiarities. The mere fact that such and such species inhabit dry, sandy places or marshes, ponds, etc., does not necessitate the plants in question to be considered as either xero- or hydro-philous species; their internal structure must be carefully examined before any conclusion can be drawn, as to whether these plants are "solely adapted" to these special environments. As regards our species of Fimbristylis it might seem very tempting to classify these in this way: F. capillaris, F. Warei, F. stenophylla and F. ciliatifolia as xerophytes, and the remaining species as hydrophytes, but their anatomical structure does not seem to justify any such classification. In order to facilitate the anatomical comparison of the material, which we have examined, it may be well to enumerate the various localities as follows: F. autumnalis was collected in wet sandy or clayish soil in the vicinity of Washington, D. C., and in low sandy places near Eustis, subtropical Florida; F. castanea was from brackish marshes near the coast of Maryland; F. spadicea and F. puberula both from wet, sandy soil near Eustis, Florida; F. laxa from low meadowland, rather dry soil, near Brookland. D. C., as well as from low, sandy soil near Eustis, Florida; F. thermalis from hot sulphur springs near Golkonda, Nevada; F. capillaris from dry, sandy soil near Washington, D. C., and Eustis, Florida; F. ciliatifolia from dry, sandy fields in Alabama, and finally F. stenophylla and F. Warei from dry, sandy soil in the High-Pine-woods near Eustis, Florida. Besides these we have, also, examined some specimens of F. complanata and F. capillaris from Montevideo, Uruguay, which together with a number of other *Cyperaceae* were presented to the writer through the courtesy of Professor Arechavaleta, Director of the National Museum at Montevideo.

In discussing the anatomy of the vegetative organs of these species, we will begin with

#### The leaf.

By its greater ability to vary, the leaf appears to illustrate the species better than the stem or root. Considering the mere outline of the leaf, three types are readily distinguished:

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(1) the relatively broad and flat, as we find it in *F. autumnalis*, *F. thermalis*, *F. spadicea*, *F. puberula*, *F. complanata* and *F. laxa*; (2) the semi-cylindrical in *F. castanea* and (3) the approximately triangular in the remaining species. Very characteristic of the leaves of the first category is the more or less, but always very conspicuous, asymmetric blade, in contradistinction to those of the other species, a fact that has, also, been recorded by Rikli as common to *F. glomerata* (Nees) and *F. paupercula* (Bklr.) In *F. autumnalis* the leaf, as will be seen from the accompanying illustration (fig. 1), is flat and strictly dorsiventral; only the midrib is somewhat projecting on the lower surface of the blade, and this is due to its larger support of stereome. The upper face is perfectly smooth,



FIG. 1. Transverse section of half of the leaf-blade of F. autumnalis.  $\times$  75.

and there is nothing in the outline to indicate the peculiar position of the blade, as we have mentioned already, being placed edgewise by the twisting of the leaf-sheath. This form of leaf must not be confounded with the sword-shaped leaves of *Iriducea*, because both faces are equally well developed in *Fimbristylis autumnalis*, besides in *F. complanata*.

The leaf is more likely to be compared with that of a mature *Eucalyptus* or of our evergreen species of *Smilax*, of which the leaves show a similar position. It is strange to see that such peculiar leaf-position is said to be either "a xerophytic character of bog-plants or a natural adaptation of desert-plants." However in these species of *Fimbristylis* the leaf-blade is developed with this position immediately after germination, and we have not noticed any exceptions to this rule in specimens from less dry situations, nor in plants growing in *Sphagnum*-moss. It is a character that seems to be peculiar to these two species, but which cannot possibly be considered as having originated through any means of adaptation, since the structure is identical with that of the other species, in which the ventral leaf-face is turned towards the stem.

While the epidermis of the upper face in *F. autumnalis* consists only of one layer of large, thin-walled cells of equal width all through the blade, we find in *F. complanata* several layers, representing a typical water-storing tissue. Among the

#### T. Holm-Studies in the Cyperacea.

other species F laxa (fig. 2) comes nearest to F autumnalis, since the superior epidermis is only composed of one layer, but the leaf is much narrower and the blade is not placed edgewise; furthermore the leaves are tristichous. In F. spadicea the accompanying figure (fig. 3) shows that the epidermis has been developed in a few strata, but only in certain places, between the mestome-bundles. It is very strange that this species has often been considered as identical with F. castanea or at least as the type, since both are so very different,



FIG. 2. Transverse section of leaf-blade of F. laxa.  $\times$  75.



.FIG. 3. Transverse section of half of the leaf-blade of F. spadicea.  $\times 75$ .

when considered from an anatomical point of view. By examining the leaf of F. *puberula* (fig. 4) we notice that the upper surface is occupied by a huge mass of colorless and relative large cells, which represent an epidermis of several layers. Besides this the epidermis of the inferior surface is developed as a dense covering of long, unicellular hairs, a fact that would



FIG. 4. Transverse section of half of the leaf-blade of F. puberula.  $\times 75$ .

seem to point towards some special adaptation, "a xerophytic character developed in a hydrophilous plant"; yet the species is neither a hydrophyte or xerophyte as these terms are gen-

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erally applied. A structure similar to that of F. puberula but without hairs is to be found in F. thermalis (fig. 5), of which the writer received some excellent material from Dr. E. L. Greene. The leaf-blade is here broad and very thick from the immense layers of colorless tissue on the upper surface, the function of which cannot possibly be for the storage of water, since the specimens were growing in hot sulphur springs. F. *castanea* exhibits a very peculiar shape of leaf, this being semicylindrical (fig. 6), and of which the upper surface shows a



FIG. 5. Transverse section of half of the leaf-blade of F. thermalis.  $\times$  75.

still larger development of colorless tissue than any of the other species we have examined. It was rather surprising to find this narrow leaf developed on a species that inhabits brackish marshes, which are not liable to become dried out during the summer. It is actually the narrowest leaf we

have observed in any of the North American species of Fimbristylis, in proportion to its length, and the only species that possess approximately as narrow leaves are just those which inhabit a very dry and sandy soil: F. capillaris, F. ciliatifolia, F. Warei and F. stenophylla. The accompanying figures (figs. 7, 8 and 9) illustrate transverse sections of leaves from the latter three species.



from the latter three species, FIG. 6. Transverse section of leaf-blade and we notice at once the of F. castanea.  $\times$  75.

very narrow, almost triangular outline from the strongly projecting midrib. No large tissue for water-storage is developed in any of these species, but the cells of epidermis are on both surfaces relatively wide, and sometimes a double epidermis may be developed between the mestome-bundles, in both F, *ciliatifolia* and F. Warei. Characteristic of the leaf of F. stenophylla (fig. 9) are the double rows of diverging, pointed hairs along the margins and the ribs on the lower surface of the blade.

Although F. complanata is not a native of this country, we have examined some specimens, as stated above, from Uruguay, which were originally labeled F. autumnalis, to which it shows a very pronounced habitual resemblance. The position of the leaves are exactly the same, distichous with the blade held edgewise; besides the inflorescence is very rich-flowered. However, while we examined the anatomy we became aware of the fact, that in this respect our plant showed a leaf-structure different from that of F. autumnalis, but almost exactly like that of F. thermalis. In order to secure correct identification of this South American species, we sent specimens to Mr. C. B. Clarke at Kew, who kindly replied that the plant was Link's F. complanata var. Kraussiana. If Dr. Boeckeler had known of the structural divergencies between this and F. autumnalis.



FIG. 7. FIG. 8. FIG. 9. Leaves of F. ciliatifolia, F. Warei and F. stenophylla; transverse sections. × 75.

he would hardly have considered them as but one species, even if the outer likeness is very striking.

If we now compare the leaves, of which we have drawn some transverse sections from the middle part of the blade, it is readily seen that the outline and the structure of the upper epidermis presents certain features for distinguishing the species. Nevertheless these leaves demonstrate several intergradations, thus the various forms may be easily deducted from one another. The epidermis of the upper surface is either developed as one single layer of large, bulliform cells, or as several strata, that cover the mesophyll. None of these strata are, however, differentiated in such a way as to have the function of opening or closing the leaf, the so-called "Gelenkcellen" of the Germans, common to *Cyperacee* and *Graminee*.

In passing, to describe the minor details of the leaf-structure, we observed the cuticle to be very thin and smooth in *F. autumnalis, F. laxa* and *F. complanata*, less so in *F. spadicea*; in the remaining species the cuticle is very thick, but smooth, not granular. The epidermis of the lower surface is almost

smooth with no furrows, and consists usually of smaller cells than that of the upper, and is frequently developed into unicellular hairs or very minute spines, which are directed upwards. The stomata are restricted to the lower epidermis, where they form longitudinal rows outside the mesophyll between the mestome-bundles. Characteristic of the stomata is the deep and somewhat narrow air-chamber, which we have noticed in most of our species with the exception of F. castanea, where it is shallow and wide. The guard-cells are projecting in F. autumnalis, F. laxa, F. puberula, F. spadicea and F. complanata, but not in the other species; they are extremely thick-walled in F. castanea.

Similar to all the other *Cyperaceæ*, examined so far, silicious cones are observable in the epidermis-cells that cover the stereome. As regards mechanical support most of our species possess a well-developed stereome, the location of which can be seen on the sections, figured above. It accompanies the larger mestome-bundles as hypodermal groups on the lower surface of the blade, while on the upper it is restricted to the margin. A few thin-walled stereome-cells may be found above some of the largest mestome-bundles, but separated from these by mesophyll. Although the stereome does not form any sheaths around the mestome-bundles, it nevertheless renders a strong support to the leaf by its very thick-walled cells, and is altogether very well represented in our species of *Fimbristylis*, with the only exception of *F. autumnalis* and *F. laxa*, in which it is relatively thin-walled.

The chlorophyll-bearing tissue, the mesophyll, occupies only a small part of the leaf-blade, since it is generally traversed by a number of mestome-bundles, which are especially large in the narrow-leaved species, such as *F. capillaris*, *F. Warei*, etc. It forms a homogeneous tissue on both faces of the leaf, and the cells are true palisades, arranged radially around the mestome-bundles. Furthermore this tissue is very compact in our species excepting in *F. laxa*, of which some specimens from Florida showed wide lacunes; and *F castanea*, in which the palisade-cells are almost star-shaped, leaving numerous and quite large intercellular spaces. Tannin was observed to be very plentiful in this tissue, especially in *F. spadicea*, *F. puberula* and *F. thermalis*.

Considering the mestome-bundles, these are all arranged in a single plane in the leaves of *Fimbristylis*; they vary in proportion to size and outline, the larger being more or less oval, the smaller constantly orbicular. They are imbedded in the mesophyll, and are, as we have seen above, in no connection with the stereome, hence they are "pure" mestome bundles. Besides being surrounded by the radially arranged palisadecells, the mestome-bundles possess, also, a completely closed parenchyma-sheath of small, thin-walled cells, which contain chlorophyll. Inside of this parenchyma-sheath there is a mestome-sheath, thin-walled in *F. autumnalis* and *F. thermalis*, but more or less thickened in the other species. The peculiar "inner chlorophyll-bearing sheath," which we described in a previous article upon *Lipocarpha*,\* occurs, also, in *Fimbristylis*, and not only in the genus "sensu strictiori," but also in those American species of *Isolepis* which we have included in the former genus. We found the structure of this sheath to be identical with that of *Lipocarpha*, being composed of much larger cells than the mestome-sheath; also by being closed in the small, orbicular bundles, but interrupted in the larger



FIG. 10. Transverse section of a mestome-bundle from the leaf of *F. autumnalis*; Ep. = epidermis of the upper surface.  $\times 400$ . (fig. 10). The cell-content seems, also, to present the same deep green color as noticeable in *Lipo-carpha*.

As regards the hadrome and leptome these have, naturally, attained their highest degree of development in the largest mestomebundles, where these tissues are sometimes separated from each other by one or more layers of thick-walled mestome-parenchyma, as in F. castanea, F. puberula, F. spadicea and F. complanata. The presence of the inner, chlorophyllbearing sheath in our species of *Fimbristylis* will necessarily place the genus as a member of Rikli's "Chlorocyperacea," among which this author has not, however, enumerated any of the Isolepisspecies examined by him. Moreover the morphological and ana-

tomical diagnosis of *Isolepis*, as demonstrated by Palla, does not seem comparable with any of the North American plants which by Torrey were referred to this genus. Our species differ very much from *Isolepis* proper by their morphological characters, also by their internal structure. And even if the inner, green sheath is not a constant character to all species in certain large genera such as *Heleocharis* and *Cyperus*, as demonstrated by Rikli, it would not be correct to consider our

\* This Journal, vol. vii, p. 172.

American species as only anatomically distinct from other representatives of *Isolepis*. Our narrow-leaved species of *Fimbristylis* do not show any very important anatomical or morphological characters by which they should be considered as distinct from the others with somewhat broader leaves; they do not present any such divergencies which induced Rikli to separate his *Chlorocyperus* and *Chlorocharis* from *Cyperus* and *Heleocharis*; besides they lack the very conspicuous character: "bractea infima erecta, inflorescentiam quasi lateralem sæpissime excedens, caulem continuans" as pointed out by Bentham.

#### The stem.

The stem above-ground, which bears the inflorescence at its apex, varies from cylindrical to being almost flattened, but shows, nevertheless, a very uniform structure in our species. The singularly flattened stem of F. autumnalis (fig. 11) and F. complanata corresponds well with the flat leaves, which are turned edgewise in these species. In F. castanea, F. thermalis,



FIG. 11. Transverse section of the stem of F. autumnalis.  $\times$  60.

F. spadicea and F. puberula the outline is almost cylindrical; in F. laxa it is polyedric; in F. Warei and F. stenophylla the outline is decangular, while F. capillaris possesses a penta- or hexa-gonal stem. When compared with the leaf the stemstructure shows many analogies, but the mechanical tissue has here attained a stronger development, the mestome-bundles are arranged in several, more or less concentric, bands and the bark-cells are not arranged radially around the mestome-bundles in all the species.

While the cuticle of the stem shows the same slight variation as we noticed in the leaves, the epidermis is often more thick-walled and does not develop such dense pubescence as in the leaves. Grooves or furrows are observable in some species, but they are rather shallow and wide; thus the stomata, which are located in these, are freely exposed. We notice the same variation in the relative width of the epidermis-cells as in the leaves; besides the characteristic cones are very numerous outside the hypodermal stereome. The bark-parenchyma forms, similar to the mesophyll, a homogeneous tissue of palisadecells, which are arranged radially towards the center of the stem in the majority of our species, but not in F. capillaris, F. ciliatifolia, F. Warei and F. stenophylla. The barkparenchyma is commonly quite solid with no lacunes, but the intercellular spaces are numerous and wide in F. castanea, F. thermalis and F. puberula. It is, furthermore, to be pointed out that the bark-palisades, which border on the leptome-side of the innermost mestome-bundles in F. castanea, do not radiate towards the center of the stem, but towards the center of the bundle. Cells containing tannin were, also, observed in the stem of various species, but not so abundant as in the leaves. We have stated above, that the stereome is more strongly developed in the stem than in the leaves. This is readily noticed if we compare the leaf-section of F. castanea, for instance, with the accompanying figure of a part of its stem (fig. 12). This section shows a number of very large



FIG. 12. Transverse section of half of the stem of F. castanea.  $\times$  75.

hypodermal stereome-bundles, most of which are situated deep into the bark between the outer band of mestome-bundles. There are, also, a few scattered and very small groups of stereome on the hadrome-side of the innermost bundles. Finally in the pith itself we observed quite a number of stereome-bundles, which were not arranged in any order, and

of which only a few surrounded minute leptomatic-bundles. Similar stereome-bundles imbedded in the pith were, also, observed in F. spadicea, but not in any of the other species. where this tissue is either strictly hypodermal or may be found on the hadrome-side of the innermost mestome-bundles. The largest part of the stem is occupied by a solid pith, mostly consisting of polyedric cells, when considered in transverse sections. With the exception of F. spadicea, of which the pith contained much tannin, this matter was not observed in the pith of any of the other species.

In regard to the mestome-bundles these are more numerous in the stem than in the leaf; they may form one single and almost concentric band as in F. capillaris (fig. 13), F. Warei, F. ciliatifolia and F. stenophylla, or several as in the other species. They show exactly the same variation as those in the

leaves, and the smallest, the orbicular ones, are invariably the most numerous and located near the periphery. Inside of these may be a second band of somewhat larger bundles as in F. autumnalis, F. puberula, F. complanata, F. laxa and F. spadicea, while even a third band is present in F. castanea and F. thermalis, these two species being the most robust of verse section of the this genus in North America. The minor stem of F. capillaris. structure of the mestome-bundles is the same,

all possessing a parenchyma-, a mestome- and an inner, chlorophyll-bearing sheath; besides the relative development of the leptome and hadrome corresponds with what has been said above in the study of the leaf. There are furthermore some leptomatic bundles located in the pith, as mentioned above (fig. 14), but these were only found in one species. F. castanea. These small bundles were surrounded by a few layers of thin-

walled stereome, also by a sheath, that evidently may be identical with a mestome-sheath; no inner chlorophyllbearing sheath was observed here, since these bundles occupied an almost central position in the pith.

#### The peduncle.

The anatomical structure of the peduncles, which bear the spikes, does not differ in any essential degree from surrounded by stereome from that of the stem. In F. castanea, for verse section. instance, the peduncle is slightly com-

pressed; the pith occupies a smaller part of the section and has no bundles neither of pure stereome or with leptome.

FIG. 13. - Trans-× 75.

FIG.14. A leptome-bundle, the pith of F. castanea; trans- $\times 320.$ 



Tannin was found in both the bark and pith. The same reduction in the size of the pith was, also, observed in *F. laxa* and *F. autumnalis*; in the latter the stereome appeared to have become more developed than in the stem, forming larger groups and, also, by being more thick-walled.

## The root.

With the exception of Van Tieghem,\* Russow, De Bary and Klinge, very few authors have given account of the rootstructure in the Cyperaceae. The elaborate work of Klinge, to which we have often referred in our articles upon this order, contains a number of detailed descriptions, by which we are enabled to obtain a broad view of the general structure besides a comparison between the principal characteristics of the roots in Cyperace and Gramine. The very important character to which Klinge has called attention as one of the most reliable for distinguishing roots of Cyperaceæ from Gramineæ, the tangential collapsing of the bark-cells, this character has, also, been observed by the writer in a number of genera from this country, including *Fimbristylis*. The structure of the endodermis seems, according to our own observations, to represent a number of variations. This sheath occurs in our species of Fimbristylis with more or less thickened cell-walls; in F. castanea the thickening appears to have reached the maximum, and the individual cells look as if their lumen had almost entirely disappeared. In F. thermalis and F. stenophylla the endodermis is, also, distinctly thick-walled with a number of layers representing an O-endodermis. And in F. autumnalis, which shows a rather weak mechanical structure, the endodermis is, nevertheless, somewhat thickened, sufficiently to be characterized as an *O-endodermis*. In *F. laxa* the endodermiscells are not thickened all round, but only on the radial and inner walls in the shape of a typical U-endodermis.

In regard to the pericambium, we have only noticed this tissue as consisting of a single layer of thin-walled cells, or as in *F. castanea* of thick-walled. Otherwise the pericambium shows the same peculiarity, discussed in the works cited above, by Klinge and Van Tieghen: that it does not form a closed ring in all the *Gramineæ* and *Cyperaceæ*, but is frequently interrupted by the protohadrome. It will, however, require further observation in order to ascertain, whether this fact is common to all or only to certain genera of the *Cyperaceæ*. While Klinge has observed the protohadrome to border immediately on the endodermis, thus breaking through the

\* Van Tieghem, Ph., Recherches sur la symétrie de structure des plantes vasculaires (Annales d. sc. nat., 5th series, vol. xiii, Paris, 1870-71, p 5).

pericambium, in several species of Carex, Eriopharum, Scirpus, Heleocharis and according to Duval-Jouve, also in Cyperus globosus, C. fuscus, C. vegetus and C. serotinus, Van Tieghem did not observe this to take place in Carex brizoides. Moreover both Duval-Jouve and Klinge observed a similar separation of the protohadrome from the endodermis in various species of Cyperus and Galilea mucronata. In Carex Fraseri, as we have mentioned in a previous article, the protohadrome is, also, separated from the endodermis. The innermost part of the central-cylinder is in F. autumnalis, F. laxa and F. thermalis occupied by a single, large vessel, and several in F. castanea and F. stenophylla. The conjunctive tissue seems most often to be thin-walled, with the exception of F. castanea and F. laxa. The structure of the roots in our species of the genus does not seem to present any other mechanical protection than that rendered by the thick walled endodermis, although we should have expected to find a similar protection in the innermost layers of the bark corresponding to what we observed in Scleria and Lipocarpha with their thick-walled bark-parenchyma.

These anatomical details, which we have observed in North American species of *Fumbristylis*, seem to illustrate that we have only one genus before us; the species which by Torrey were referred to Isolepis appear to be inseparable from the others, not only from an anatomical, but, also, from a morphological viewpoint. And if we consider the various species, as we have studied them in this country, they exhibit a sufficient number of characters which may be regarded as "mutual affinities," such as these are understood in orders as large as the Cyperaceae. But it does not seem possible to draw any such distinction, as for instance to separate the species into "Xerophytes or Hydrophytes," even if the local environment might suggest these plants to belong to different "plant-societies." Because the internal structure of the stem, the leaf and the root does not furnish any evidence that certain anatomical features are necessarily dependent on a special climate or soil, neither very dry nor very damp. It seems much more natural simply to acknowledge that such and such species live under such and such conditions, even if we, on the other hand, are unable to account for the similarities and diversities in struc-The statement that bog-plants may possess xerophytic ture. characters and vice versa gives no satisfaction, and is even misleading; characters may have been simply inherited without being at present of any particular advantage to the species. The inner, chlorophyll-bearing sheath may represent a char-acter of that kind, its function being, so far, unexplainable.

This sheath is, as we have stated above, not especially characteristic of any type of *Fimbristylis*; it is common to our native species and a number from the old world. It is not restricted either to any certain shape of leaf or to species from any peculiar region or locality. Furthermore the relative development of the mechanical tissue in our genus from dry as well as from wet soil furnishes no information regarding a supposed existence of plant-societies with xerophytic or hydrophytic structures; neither the radial arrangement of the palisade-cells or the presence of a parenchyma-sheath. Hence an attempt to classify our native species of *Fimbristylis* as "xerophytes or hydrophytes" would seem very unnatural and not in conformity with their biological peculiarities.

Brookland, D. C., December, 1898.

# ART. XLIX.—On Roscoelite; by W. F. HILLEBRAND and H. W. TURNER, with a note on its chemical constitution by F. W. CLARKE.

# ANALYSIS AND COMPOSITION, BY W. F. HILLEBRAND.

THE rare mineral roscoelite has greatly needed reëxamination in order to reconcile the discrepancies between the analyses of Roscoe and Genth and to establish a satisfactory formula for this supposed vanadium mica. To the kindness of Mr. G. W. Kimble of Placerville, Cal., I am indebted through Mr. H. W. Turner for specimens from the Stockslager mine, from which a limited amount of fairly pure material was picked out. This was then laboriously purified by the aid of Thoulet's solution, the result being a very nearly pure product weighing only 1.2 grams and having after drying at 100° C. a density of 2.97 at 20° C.

Notwithstanding the small amount, it was possible by the exercise of care to make fairly satisfactory analyses.

With regard to the methods employed little need be said except as to the determination of the condition of the vanadium. For this purpose decomposition was effected by rather dilute  $H_2SO_4$  in sealed tubes, the greatest care being taken to expel every trace of air from the powder and acid and to seal the tube during passage of a current of  $CO_4$ . Otherwise it is impossible to prevent oxidation of a considerable part of the  $V_2O_4$ . In one case, unfortunately, the air cannot have been fully expelled, for the solution after decomposition was blue instead of green and much less oxygen was required in titration than when the color was green.

The contents of the tube, still warm, were poured into fairly hot freshly boiled water and titrated rapidly. Iron and vanadium were then reduced by  $H_sS$  gas, the latter boiled out in a current of  $CO_s$ , and titration repeated on the hot liquid. The solution was then boiled with ammonia, the precipitate fused with Na<sub>2</sub>CO<sub>3</sub>, leached with water, and the residue again fused with Na<sub>2</sub>CO<sub>3</sub> and leached to remove the last of the vanadium. This residue was then fused with KHSO<sub>4</sub>,<sup>\*\*</sup> dissolved in dilute  $H_sSO_4$ , boiled first with  $H_sS$  and then in a current of  $CO_2$ , and the liquid titrated for total iron. The solution held titanium which was then estimated colorimetrically.

The first of the titration results gave the effect of all iron, assuming its existence as FeO, and of all vanadium that might

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<sup>\*</sup> Any slight trace of vanadium remaining will impart a bright yellow color to the cold KHSO<sub>4</sub> fusion, a test which proved useful more than once during the analysis.

### Hillebrand, Turner and Clarke-Roscoelite.

exist in a lower state of oxidation than  $V_{3}O_{3}$ . The second gave all iron as FeO and all vanadium as  $V_{3}O_{4}$ . Deduct from both the figure for FeO and the remainder gives that for vanadium. In this way two very concordant results were obtained for total vanadium as  $V_{2}O_{4}$ , which were supplemented by tests on portions used for other constituents, but only one was obtained for the vanadium as it exists in the mineral, a second being vitiated by evident oxidation during decomposition in the tube. As a check, however, a fresh sample of unpurified mineral was similarly treated and it was found that fully nine-tenths of the vanadium existed as  $V_{2}O_{3}$ , a result confirming the single test on the purified material which showed 93.5 per cent as  $V_{2}O_{3}$ . It is not impossible that slight oxidation had taken place even in these cases, and I feel justified in assuming with Genth that the vanadium should be considered wholly as  $V_{3}O_{3}$ .

In the other portions analyzed the vanadium was likewise titrated in  $V_2O_4$  condition, but only after separation from iron, titanium and aluminum by fusion with Na<sub>2</sub>CO<sub>3</sub>, extraction with water and separation of dissolved alumina by ammonium carbonate. A second fusion of the residue and of the precipitated alumina was necessary in order to extract all the vanadium. These numerous manipulations render the figures for Al<sub>2</sub>O<sub>3</sub> perhaps the least trustworthy of all, but the average given is probably not far from correct.

The iron is assumed to be present as FeO; and the titanium to belong to a foreign mineral, since a test on unpurified material gave much more, namely, 1.50 per cent TiO<sub>2</sub>, without accompanying increase in FeO, which latter observation seems to exclude ilmenite as the source of the titanium.

Both the iron and magnesium are supposed to belong to the roscoelite, since they were found by Genth in nearly the same amounts and no recognizable iron or magnesium minerals were noticed in the purified powder.

For comparison, the mean of Roscoe's analyses and that one of Genth's considered by himself to be his best are also given in the table on the following page.

Very marked differences are apparent in the three analyses by different chemists. If titanium was present in the material analyzed by Genth and Roscoe, as is very probable, their high results for alumina are in great part at least accounted for. It is inconceivable how Genth obtained his value for water by ignition, since the mineral oxidizes when heated in air. In fact the oxidation in one of my own analyses, after allowing for loss of water as ascertained by direct weight, was almost what theory requires for the oxidation of  $V_2O_3$  to  $V_2O_3$  and of FeO to Fe<sub>2</sub>O<sub>3</sub>, or 5.14 per cent instead of 5.27 per cent. It

may fairly be assumed that his water was weighed directly after expulsion by ignition of the powder. Roscoe's figures for water, if not for moisture, must be affected by error, probably arising from the unsuspected oxidation of vanadium.

Amount used.	Hillebrand.						Conth	Degees	
	·3000g.	·2531g.	··2635g.	·1560g.*	·2038g.	Mean.	Gentin.	Noscoe.	
$\begin{array}{c} {\rm SiO}_{2} \\ {\rm TiO}_{2} \\ {\rm V}_{2}{\rm O}_{3} \\ {\rm Al}_{2}{\rm O}_{3} \\ {\rm FeO} \\ {\rm FeO} \\ {\rm MgO} \\ {\rm Na}_{2}{\rm O} \\ {\rm Li}_{3}{\rm O} \\ {\rm H}_{2}{\rm O} \ {\rm below} \\ {\rm 105^{\circ}C} \\ {\rm H}_{2}{\rm O} \ {\rm below} \\ {\rm 105^{\circ}C} \\ {\rm H}_{2}{\rm O} \ {\rm above} \\ {\rm 280^{\circ}C} \\ {\rm Fl} \\ {\rm SiO} \\ {\rm C} \\ {\rm Fl} \end{array}$	45:30 .77 23:90 1.59 1.64 .40 .17	45.04 24.00 11.74 10.41 .13 ft. tr.	·77 11·34 10·32 none 4·29	24:09 1:65	-80 24:06 1:57	45.17 .78 24.01 11.54 1.60 1.64 10.37 .06 ft. tr. .40 .17 4.12 none	47.69 20.56 14.10 1.67 2.000 7.59 .17 tr.	SiO2	41:25 28:60 14:14 1.13 1.15 .61 2.01 8:56 .82 1.08 2:27 101:62

ANALYSES OF ROSCOELITE.

From the column of means of my own analyses the following ratios are obtainable :

SiO,	.753
V.O.	.159
AĴ,Ŏ,	·113
FeO	.022
MgO	·041
K <sub>0</sub> O	.110
Н,О	.229

The entire absence of manganese and of calcium in my own and Genth's samples tends to confirm the suspicion that Roscoe's material was far from pure. It is to be remarked, however, that my figures for vanadium agree quite closely with his and differ widely from Genth's.<sup>‡</sup>

Discrepancies of this kind are not necessarily to be ascribed to faulty analyses. It is well enough known that in any one

\*4.94 per cent oxygen used for complete oxidation instead of 5.27 needed for all V as  $\rm V_2O_3$  and Fe as FeO.

 $\dagger$  Equivalent to 23.59 per cent  $V_2O_3.$   $\ddagger$  This agreement is probably more apparent than real for the reason that Roscoe's figure would be materially lowered by regarding the iron of his analysis as FeO instead of Fe<sub>2</sub>O<sub>3</sub> in conformity with my analysis.

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species of mica various molecules must sometimes be assumed to exist in different proportions and the general formula for such a species can only be arrived at by comparison of a series of analyses of different varieties. Hence, in view of the lack of any simple ratios, the deduction of a definite and final formula from my data is not justifiable. Further analyses are needed of new and very pure material from other locations even if these be not far removed from the source of the present material. Nevertheless, in the hands of an expert very unpromising data may often be made to afford positive indications, and that this is true in the present case the following discussion by Professor F. W. Clarke clearly shows.

## CHEMICAL CONSTITUTION OF ROSCOELITE, BY F. W. CLARKE.

The ratios given in the foregoing new analysis, used directly, lead to the following empirical formula for roscoelite :

# H<sub>458</sub>K<sub>220</sub>Fe<sub>22</sub>Mg<sub>41</sub>Al<sub>226</sub>V<sub>318</sub>Si<sub>753</sub>O<sub>2724</sub>.

Here H to K, and Mg to Fe are as 2 to 1. Between O and Si, however, the ratio is not simple, and lies below the orthosilicate and above the trisilicate proportion. Since in many micas the groups  $SiO_4$  and  $Si_3O_8$  are replaceable, that suggestion may be followed out here; and then the formula reduces to

# $R'_{676}R''_{63}Al_{226}V_{316}(SiO_4)_{536}(Si_3O_6)_{71}$ .

From this expression, applying Clarke's mica theory, the mineral may be regarded as a molecular mixture of the three compounds

1.	2.	3.
$\sim$ SiO $\equiv$ FeK	$\sim Si_0O_0 \equiv KH_0$	$sio_{i} \equiv KH_{s}$
Al-SiO MgH	$Al = Si_0 = KH_1^2$	$Al = SiO_{4}^{*} \equiv V^{*}$
SiO $=$ MgH,	Si $O$ $\equiv$ Al, $1$	$\operatorname{SiO}_{=}^{*} = V,$

in the ratio 21:22:159, or nearly 1:1:8. Upon reducing the analysis to 100 per cent, after throwing out the TiO<sub>2</sub> and the water lost below  $280^{\circ}$  as extraneous, we get the following comparison between the results found and the theoretical composition.

	Found.	Reduced.	Calculated.
SiO,	45.17	45.88	45.52
TiO	•78		
V.O.	24.01	24.39	24.64
Al <sub>0</sub> 0,	11.54	11.73	11.62
MgO	1.64	1.66	1.72
FeO	1.60	1.63	1.55
К.О	10.37	10.53	10.81
$H_0O, 280^\circ - \dots$	•57	·	
" 280° +	4.12	4.18	4.14
-		·	
	99.80	100.00	100.00

This comparison, based on the ratio 21:22:159, is as satisfactory as could be expected.

Of these component molecules, the first represents the normal phlogopite type: the second is a trisilicate alkaline biotite; and the third, which forms 74.5 per cent of the whole mass, is a muscovite in which two-thirds of the aluminum have been replaced by vanadium; in short, a vanadium muscovite. Ordinary muscovite is Al<sub>a</sub>(SiO<sub>4</sub>)<sub>3</sub>KH<sub>2</sub>; and whether a corresponding V (SiO ), KH, exists, can be determined only by analyses of roscoelite from other localities, and so learning its range of variation. That vanadium may replace aluminum is shown by the fact that Piccini has prepared true vanadium alums. That roscoelite is essentially a vanadium muscovite seems to be fairly well established. As for the molecule Al<sub>a</sub>(Si<sub>a</sub>O<sub>a</sub>)<sub>3</sub>K<sub>2</sub>H<sub>4</sub>, its existence is indicated in some other micas; and in Simmler's "helvetan" it seems to be the dominant molecule.

#### THE OCCURRENCE OF ROSCOELITE, BY H. W. TURNER.

According to H. G. Hanks,\* at one time State mineralogist of California, attention was first called to roscoelite by Dr. James Blake at a meeting of the San Francisco Microscopical Society, July 2d, 1874. The specimens then exhibited were from the Stockslagert mine, which is about 1<sup>klm</sup> southwesterly from Lotus on Granite Creek in Eldorado County.

At a meeting of the California Academy of Sciences held July 20, 1874, Dr. Blake presented specimens of the same mineral, which he then supposed to be a chromium mica.

At a meeting of the California Academy held August 2, 1875,<sup>‡</sup> Dr. Blake read a paper on roscoelite. Samples sent by him to Dr. Genth of Philadelphia were found to contain vanadium. The mineral was named by Blake in honor of Professor Roscoe of Manchester, England, who had made vanadium a special study. Dr. Blake calls attention to the fact that Dr. Hall found vanadium widely diffused in many rocks, generally associated with phosphorus. According to Hanks the Stockslager vein from which the roscoelite obtained by Dr. Blake was taken, is small and not continuous, varying from two inches to a foot in thickness and running nearly parallel with Granite Creek. Associated with the quartz is calcite, and there are at least two varieties of iron sulphide present, probably pyrite and chalcopyrite. Hanks states further that the gold occurs only with the roscoelite and is

<sup>‡</sup> Proceedings Cal. Acad., vol. vi, p. 150, 1875

<sup>\*</sup> Second Ann. Rep. State Mineralogist of California, pp. 263-4, 1880-2. † According to Lindgren (see Economic Sheet of the Placeville folio of the Geol. Atlas of the U.S.) this name should be spelled as above, but Hanks spells it Stuckslager.

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found interstratified with the roscoelite laminæ in pieces from the value of one dollar to the minutest microscopic particles. He also states that from four to five hundred pounds of roscoelite were obtained by the miners, all of which was wasted in extracting the gold.

Mr. George W. Kimble of Placerville, California, for many years county surveyor, has furnished the California material analyzed by Dr. Hillebrand as well as other specimens. In these specimens the roscoelite is in part embedded in quartz and probably contemporaneous in formation with the quartz, and in part fills little cracks in the quartz and therefore somewhat later.

There are given below four localities where roscoelite has been found, according to Mr. Kimble, to whom the author is indebted for the following information about the occurrence of the mineral at these localities.



FIG. 1. Geological map copied from the Placerville folio, showing roscoelite localities. Geology by W. Lindgren.

The accompanying map, on the scale of about 1-150000, gives the exact localities where the roscoelite has been found. The Calaveras formation is largely of Carboniferous age, as may also be the augite porphyrite tuff associated with it. The serpentine is later than the Calaveras formation and earlier than the granodiorite, which is probably late Jurassic or early Cretaceous. It will be observed that all of the localities are at or near the contact of an intrusive granodiorite mass with the surrounding rocks, chiefly sediments and older lavas. This suggests that the mineral may be regarded as in some way due to the mineralizing solutions accompanying the intrusion of the gran-However, the quartz veins clearly fill fractures odiorite. which formed in the granodiorite and associated rocks after the consolidation of the granodiorite; consequently the deposition of the quartz and the associated gold and roscoelite must have been also subsequent to the consolidation of the granodiorite. The following are the localities reported by Mr. Kimble. They are all in Eldorado County, from 8 to 15kim northwest of Placerville.

Locality 1. Thompson Hill on its northeast slope about 2.5<sup>klm</sup> southeast of the Stockslager mine. — There are here fifteen or more small seams of quartz having a strike of north of west. As these seams pass through the contact of the granodiorite with the greenstone (augite-porphyrite?) they contain rich spots of gold and roscoelite. The seams of quartz pass on through the northeast point of Thompson Hill and come into the granodiorite again.

Locality 2. Stockslager mine on Granite Creek. — Mr. Lindgren informs me that the vein of the Stockslager mine is in a narrow wedge of metamorphic sediments of the Calaveras formation. Immediately east of this wedge is granodiorite, and immediately west is serpentine. Mr. Kimble states that there is here but one vein of quartz. This passes from the granodiorite into the narrow wedge of the Calaveras formation. It does not penetrate the serpentine. As previously stated, it was at this locality that by far the larger part of the roscoelite was obtained, including that analyzed by Dr. Hillebrand.

Locality 3. South slope of spur about 2.7<sup>klms</sup> north of the village of Lotus.—In micaceous slate, which is part of a contact metamorphic zone of the Calaveras formation. The exact locality is about 500 feet east of the contact. It has never been demonstrated, but Mr. Kimble thinks that this quartz vein extends southeast into the granodiorite.

Locality 4. Clark Mountain on its east slope at the contact of the Calaveras formation and the granodiorite.—The occurrence here is identical with that at the Stockslager mine.

According to Kimble no roscoelite has ever been found where the seams are in granodiorite, and the latter is not altered; but some has been found at the contact of the quartz with serpentine in localities 2 and 4. All of the quartz seams at localities 1, 2, and 4 dip southwest and have pockets of gold. Prof. Hanks<sup>\*</sup> states that roscoelite was also found in Sec. 31, T. 11 N. Range 10 E, two miles from the Stockslager mine. This appears to be the Thompson Hill locality of Kimble, to whom, indeed, Prof. Hanks was probably indebted for his information. Hanks states that the roscoelite was found here in the bed rock of Big Red ravine in a dark-colored micaceous rock in small seams of quartz with calcite and gold.

The roscoelite from California shows a tendency to crystallize in little rosettes, so that individual scales of any size with the same optical orientation throughout are difficult to obtain. Some scales gave with convergent light a nearly uniaxial black cross, the hyperbolas opening but slightly on rotation, indicating a small axial angle. Like all other micas it is optically negative. The pleochroism as seen in thin foils is, c and b clove brown to greenish yellow brown, a light greenish yellow. In the scales of the powder analyzed no rutile needles or other inclusions were detected, but in the center of a rosette of roscoelite scales were found dark grains with a metallic luster. These grains are of sufficient size to have fallen with the heavy minerals during the process of separation with the Thoulet solution, and it is not likely that any of them have been included in the powder analyzed, although they were noted in the impure material before it had undergone the final separation. The grains show no crystal form and were not determined.

\* Loco citato, p. 263.

# ART. L.—On Gravitation in Gaseous Nebulæ; by FRANCIS E. NIPHER.

THIS subject has received attention of late through the work of Dr. See, who has rediscovered the law announced by Ritter in 1878. According to Ritter, if R be the radius of a spherical mass of gas of cosmical dimensions, and T its temperature, the product TR = constant. As Ritter announced, the heat capacity of such a gravitating mass is negative. If heat leaves the gas, it contracts and becomes warmer. Dr. C. M. Woodward has recently published a paper\* in which he deals with the conditions of equilibrium in such a mass, and he deduced the equation for the mass of the central core of a gravitating spherical nebula

$$\mathbf{M} = \frac{2\mathbf{CT}_{o}r}{\mathbf{K}}$$

Here C is the constant for the gas, and M is the mass internal to any radius r. K is the gravitation constant and  $T_o$ is the constant temperature of the mass. Woodward admits that if such a mass could be contracted, its temperature would rise, but he denies that gravitation is competent to contract the gas, and even concludes that such a nebula cannot lose heat by radiation.

The present writer, in the succeeding number of the Transactions, has shown that such contraction is possible; and that when T is made variable in the above formula, the value of Ritter's constant is determined by that equation, in terms of the gravitation constant, the constant for the gas, and the mass M internal to r.

This equation is then applied to a cosmical mass of hydrogen. What must be the physical condition in order that a central mass or core, having a radius equal to that of the sun, should contain a mass equal to that of the sun. The conditions of the problem determine r, C and M; and K being known, the value of T turns out to be 20,000,000 degrees centigrade. The pressure at the surface of this sphere is computed, and it is found to be  $3.706 \times 10^{14}$  dynes per square centimeter, or 366,000,000 atmospheres. The average density of the spherical mass, which is three times the density at the surface of the hydrogen sun, is about 7 per cent less than the average density of the sun itself. The pressure at a distance of 92 million miles from the center of mass is found to be about 0.4 of an atmosphere.

\* Trans. Acad. of Sci. of St. Louis, vol. ix, No. 3.

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The equations show that the same pressures and densities would hold for any other perfect gas. In fact, the above equation shows that if r and M are fixed, the product TC must be constant for all gases. This carries with it the conclusion shown by the other equations, that the average density of such a solar mass is independent of the nature of the gas. This is a matter of great significance, when taken in connection with the fact that the real density of the sun is only slightly greater than the density of the hypothetical hydrogen sun.

The real condition around our sun is, that increasing opacity to radiation as one goes to levels of smaller radius, has retained the heat within the dense nucleus. The rarefied external parts of the solar nebula have parted with their heat and the temperature throughout the mass has ceased to be uniform. Interplanetary pressures have been abolished. Hydrogen would solidify at a distance of 92 million miles from our sun if away from any large mass of matter. And this obliteration of cosmical pressure has almost wholly compensated the fall in temperature of the sun from 20 millions at least to perhaps 10,000 degrees.

The fact that a gaseous mass can apparently contract itself, and heat up in some such way as it would do if it were compressed by the action of some external system, is obviously of profound significance. The clue that it seems to give concerning the nature of gravitation is well worthy of the most serious attention. Is not gravitation the action upon matter of a system wholly external to matter?

## ART. LI.—The Titration of Oxalic Acid by Potassium Permanganate in presence of Hydrochloric Acid; by F. A. GOOCH and C. A. PETERS.

[Contributions from the Kent Chemical Laboratory of Yale University-LXXXII.]

LÖWENTHAL and LENSSEN\* were the first to show that the titration of a ferrous salt by potassium permanganate in the presence of hydrochloric acid, according to the process of Margueritte<sup>+</sup> is vitiated by the evolution of chlorine outside the main reaction, and to point out that a remedy for the difficulty is to be found in the titration of the ferrous salt in divided portions, other equal volumes of the ferrous solution being added to the liquid in which the first titration is accomplished until the amount of iron indicated by successive titrations becomes constant.

Kessler<sup>‡</sup> showed the restraining influence of certain sulphates, of manganous sulphate in particular, upon the irregular and undesirable interaction of the permanganate and hydrochloric acid, and Zimmermann,§ in apparent ignorance of Kessler's forgotten proposal, advocated the introduction of a manganous salt, best the sulphate, into the ferrous salt to be determined, thus accomplishing the purpose of the empirical procedure of Löwenthal and Lenssen.

The tendency toward evolution of chlorine in the oxidation of a ferrous salt by permanganate, as compared with the absence of such tendency in the similar oxidation of oxalic acid, in presence of hydrochloric acid, was explained by Zimmermann on the hypothesis that an oxide of iron higher than ferric oxide is formed as an intermediate product, and that this unstable oxide is sufficiently active to break up hydrochloric acid as well as to oxidize more of the ferrous salt. Quite recently, Wagner finds explanation of the sensitiveness of the hydrochloric acid solution of the ferrous salt in the probable formation of chlor-ferrous acid (analogous to chlorplatinic and chlor-auric acids), which suffers oxidation more readily than hydrochloric acid under the action of the permanganate. The protective influence of the manganous salt turns apparently, as Zimmermann suggested, upon the initiation of Guyard's reaction, according to which the permanganate and manganous salt interact to form a higher oxide of manganese of a constitution approaching the dioxide more or less closelythis oxide being capable of oxidizing the ferrous salt, but slow

S Ann. d. Chem., ccxiii, 302.

Maasanalytische Studien, Habilitationsschrift, Leipzic, 1898.

to act upon the hydrochloric acid, or the chlor-ferrous acid of Wagner. According to Volhard\* the reaction of Guyard is favored and hastened by heat and concentration of the solution, while it is delayed by acidity and dilution; but even in solutions containing very little manganous salt and a considerable quantity of free acid the faint rose color developed by the careful addition of permanganate ultimately vanishes until every trace of the manganous salt is precipitated. When a considerable amount of the salt is present interaction follows immediately the introduction of the permanganate. Zimmermann advocates the use of 4 grams of manganous sulphate uniformly in titrations of a ferrous salt by permanganate, a procedure to which Wagner gives acquiescence, though pointing out that a ninth of that amount is all that he finds to be necessary. The excess of the manganous salt can do no harm so long as the higher oxide, the product of interaction of the manganous salt and the permanganate, is immediately reduced by even traces of a ferrous salt, and this appears to be the case at least within the limits proposed by Zimmermann and Wagner. Thus we find, as shown in results of the accompanying table, that so much as five grams of the sulphate may be present in 135cm3 of the liquid, containing about 5cm3 of hydrochloric acid of full strength, without interfering with the regularity of the titration; and the effect is trivial even when the amount of manganous sulphate reaches ten grams. We find also practical regularity of working when manganous chloride is substituted for the sulphate, and in this respect our results accord with those of Zimmermann and differ from those of Wagner:+

Cotal volume					
t beginning	HC1		KMnO <sub>4</sub>		
of titration.	Sp. gr. 1.09.	FeCl <sub>2</sub> .	$\frac{1}{10}$ N.	$MnSO_4.5H_2O.$	$MnCl_2 \cdot 4H_2O$ .
cm <sup>3</sup> .	$cm^3$ .	cm <sup>3</sup> .	cm <sup>3</sup> .	grams.	grams,
135	10	25	21.70	1.	
135	10	25	21.70	3.	
135	10	25	21.70	5.	
-135	10	25	21.75	7.	
135	10	25	21.75	10.	
145	20	25	21.75	10.	
175	50	25	21.75	10.	
135	10	25	21.70		1.
135	10	25	21.70		2.
145	20	25	21.70		2.
155	30	25	21.75		3*
165	40	25	21.70		4.

In all cases, however, in which the larger amounts of manganous salt are present, the end reaction is marked by the advent

\* Ann. d. Chem, exeviii, 318, 1879. + Loc. cit., p. 104.
of a brownish red precipitate rather than the clear pink of the soluble permanganate, and it is obvious that in case the solutions to be oxidized were not active enough to act with rapidity upon the product of the Guyard reaction, difficulty might follow the failure to adjust the conditions more particularly.

It has been stated by Fleischer\* and Zimmermann+ that hydrochloric acid interferes in no way with the titration of oxalic acid by potassium permanganate. This statement, however, is not in accord with our experience; for we find that in such titrations there is a small though real waste of permanganate proportionate to the amount of hydrochloric acid present. This fact is brought out clearly in the comparison of experiments of section A in the following table, in which no hydrochloric acid was present, with experiments B, in which hydrochloric acid was present.

Temp	erature at be	ginning abou	t 80° C.	
		Ammonium		Variation from
$H_2SO_4$	HCI	oxalate		mean of A taken
$\cdot 1:1$	Sp. gr. 1.09.	$\frac{1}{10}$ N.	KMnO <sub>4</sub> .	as standard.
cm <sup>3</sup> .	$cm^3$ .	cm <sup>3</sup> .	cm <sup>3</sup>	cm <sup>3</sup> .
		A		
5		50	47.50	0.00
5		50	47.50	0.00
10		50	47.50	0.00
10		50	47.50	0.00
25		50	47.50	0.00
25		50	47.50	0.00
		В		
10	2.5	25	23.80	+0.02
10	2.5	25	23.90	+0.12
10	5.0	25	23.90	+0.12
10	10.0	25	24.00	+0.25
5		25	23.80	+0.05
10	10.0	25	24.00	+0.25
10	10.0	25	24.10	+0.35
	$\begin{array}{c} Temp\\ H_2SO_4\\ \cdot 1:1\\ cm^3,\\ 5\\ 5\\ 10\\ 10\\ 25\\ 25\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10$	Temperature at be        H <sub>2</sub> SO <sub>4</sub> HCl        1:1      Sp. gr. 1·09.        cm <sup>3</sup> .      cm <sup>3</sup> .        5         10         25         10      2·5        10      2·5        10      2·5        10      2·5        10      5·0        10      10·0        5         10      10·0        10      10·0	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Temperature at beginning about 80° C.        Ammonium        H <sub>2</sub> SO <sub>4</sub> HCl      oxalate        1:1      Sp. gr. 1'09. $\frac{1}{10}$ N.      KMnO <sub>4</sub> .        cm <sup>3</sup> .      cm <sup>3</sup> .      cm <sup>3</sup> .      cm <sup>3</sup> .        5       50      47:50        10       50      47:50        10       50      47:50        25       50      47:50        25       50      47:50        25       50      47:50        0      2:5      25      23:80        10      2:5      25      23:90        10      5:0      25      23:90        10      10:0      25      24:00        5       25      23:80        10      10:0      25      24:00        5       25      24:00        10      10:0      25      24:00

From these results it is evident that, though the error introduced by the presence of the hydrochloric acid during the action of the permanganate upon the oxalic acid is small, it is plainly appreciable. The questions arise, therefore, first, as to whether the secondary action of the permanganate upon the hydrochloric acid may be prevented by the presence of a suitable amount of a manganous salt, and, secondly, as to whether in this event the reducing agent,—the oxalic acid—is sufficiently active, like the ferrous salt, to prevent the premature establishment of an end color due to the Guyard reaction. The latter question must naturally be settled before the former can

\* Volumetric Analysis; Trans. by Muir, p. 71. + Loc. cit.

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be taken up. In the accompanying table are recorded the effects of varying amounts of manganous salt in presence of different amounts of sulphuric acid in the reaction of permanganate upon oxalic acid.

	$Tem_{f}$	perature at	beginning about .	80° C.	
Volume	$H_2SO_4$	Ammonium	N CO FT O	TTAL	Variation
at beginning.	1:1.	oxalate.	$MnSO_4.5H_2O.$	$KMnO_4$ .	irom
(120	- Cm <sup>-</sup> .	10% Cm .	grams.	00.55	stanuaru.
130	5	20		23.75	0.00
130	. 9	25	0.0008	23.75	0.00
1 1 3 0	5	25	0.0032	23.75	0.00
130	5	25	0.0160	23.75	0.00
- 7 <u>1</u> 30	ð	25	1.	23.70	-0.02
130	5	25	2.	23.75	0.00
130	5	25	2.5	23.60	-0.12
130	5	25	3.0	23.40	-0.22
[ 130	5	25	4.0	23.60	-0.12
(500 .	5	25		23.80	+0.02
500	5	25	0.0008	23.80	+0.02
500	5	25	0.0032	23.80	+0.05
$\frac{1}{500}$	5	25	1.	23.70	-0.02
500	5	25	2.	23.40	-0.32
500	5	25	3.	23.50	-0.22
( 500	5	25	4.	23.30	-0.42
(130	( 10	25	1.	23.80	+0.05
130	] 10	25	2.	23.75	0.00
130	] 10	25	3.	23.65	-0.10
. 130	$\left( 10 \right)$	25	4.	23.50	-0.22
130	(15	25	2.	23.75	0.00
130	$\{15$	25	4.	23.70	-0.02
130	(15	25	5.	23.50	-0.52
130	( 30	25	2• .	23.75	0.00
130	$\{ 30 \}$	25	4.	23.70	-0.02
(130	1 30	- 25	5.	23.75	0.00

From the results given it is evident that the persistence of the Guvard reaction is liable to interfere with the end reaction of oxidation of oxalic acid unless an adjustment is made between the quantity of the manganous salt, the amount of acid, and the dilution. In hot solutions of a total volume of 130<sup>cm<sup>3</sup></sup> at the beginning, no more than 2 grams of the manganous sulphate should accompany 5 to 10ems of the 1:1 sulphuric acid; when the total volume at the beginning reaches 500<sup>cm<sup>3</sup></sup>, no more than a single gram of the salt should be present with  $5^{cm^3}$  of the 1:1 sulphuric acid. The amount of manganous salt may, however, be increased considerably if the quantity of acid is increased.

As Kessler has noted, a sufficiency of the manganous salt, acting no doubt as the medium of transfer of oxygen, may bring about interaction between the permanganate and the oxalic acid at atmospheric temperatures without the tedious delay ordinarily encountered in the attempt to consummate that action in cold solutions. It would seem natural that the manganic hydroxide formed in the Guyard reaction at low temperatures should yield more readily to the reducing action of the oxalic acid than the more anhydrous form to be expected in hot solutions, so that at such temperatures the limits as to proportions of manganous salt, acid, and dilution, within which favorable action may take place, should be wider; moreover, the undesirable action of the permanganate upon hydrochloric acid, when that acid is present, should be less appreci-able at lower temperatures. In our experiments, therefore, upon the oxidation of oxalic acid by potassium permanganate in presence of hydrochloric acid, we have studied the effect of varying the proportions of the manganous salt both at atmospheric temperatures and the higher temperatures generally employed.

	1		1	Ammo-					
Number	Volume		HCl	nium				Variation	
of	at begin-	$H_2SO_4$	Sp. gr.	oxalate		$MnSO_4$ .	MnCl <sub>2</sub> .	from	
experi-	ning of	1:1	1.09.	$\frac{1}{10}$ N.	KMnO <sub>4</sub> .	$5H_{2}O.$	$4H_{2}O.$	standard.	
ment.	titration.	cm <sup>3</sup> .	$cm^3$ .	$\mathrm{cm}^{3}$ .	$\mathrm{cm}^{3}$ .	grams.	grams.	cm <sup>3</sup> .	
- 1	130		10	25	23.90	·0040		+ 0.15	
2	130		10	25	23.90	.0120		+0.15	
3	130		10	25	23.80	.0250		+0.05	
4	130		10	25	23.75	.0400		+0.00	
5	130		10	25	23.76	.0500	·	+0.01	
6	130		10	25	23.70	.1000		-0.02	
7	130		10	25	23.75	.2000		0.00	
8	130		10	25	24.20		.0200	+0.45	
9	130		10	25	23.95		.0200	+0.50	
10	130		10	25	23.80		·0400	+0.02	
11	130		20	25	23.75		·0400	0.00	
12	130		30	25	23.75		·0400	0.00	
13	130	1	10	25	23.75	1.0000		0.00	
14	130		10	25	23.75	2.0000		0.00	
15	130		10	25	23.75	3.0000		0.00	
16	130	1		25	23.72		1.0000	-0.03	
17	130	1		25	23.74		2.0000	-0.01	
18	130	1		25	23.72		3.0000	-0.03	
19	130	2		25	23.70		0.2000	-0.02	
20	130	. 3		25	23.75		0.2000	0.00	
Temperature about 80°.									
			1000	0.5	00.00				
21	145	10	10	25	23.90	0.2000		+0.15	
22	145	10	10	25	23.70	1.0000		-0.05	
23	500	10	10	25	23.75	1.0000		0.00	
24	500		10	25	23.70	1.0000		-0.02	
25	500		10	25	24.10	0.2000		+0.35	

Temperature 20°-26° C.

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From these results it appears that the presence of a suitable amount of manganous salt-either the sulphate (exps. 4-7, 13-15, 22-24) or the chloride (exps. 10-12, 16-20)—is capable, either in cold solution (exps. 1-20) or in hot solution (exps. 22-24) of preventing the action of the permanganate upon the hydrochloric acid. It appears, also, that, for a given dilution and strength of acid, less manganous salt is needed in the cold solution (exps. 4-7) than in the hot solutions (exps. 22-24). Thus, in the hot solution, at a dilution of 145<sup>cm<sup>3</sup></sup> to 500<sup>cm<sup>3</sup></sup> 1 grm. of manganous sulphate must be present with 5<sup>cm<sup>s</sup></sup> of strong hydrochloric acid, with or without sulphuric acid; while in the cold solution 0.04 grm. of either the sulphate or chloride is enough to secure adequate protective effect. Experience showed, however, that 0.5 grm. or 1.0 grm. of the manganous salt should be present in order to push the reaction with reasonable speed in cold solutions.

Wagner\* has made record of the increased evolution of chlorine in oxidations of ferrous chloride by potassium permanganate in presence of various salts, of which barium chloride was the most active. We have made some experiments, therefore, to determine whether such action would appear in the oxidation of oxalic acid in cold solutions containing certain salts, and, if so, whether it would be preventable by the presence of the manganous salt under our conditions of working. From the results given in the accompanying table, it is plain that the evolution of chlorine in cold solutions is less in the presence of these salts than when hydrochloric acid is used without them, and that such evolution may be entirely prevented (within the proportions of our work) by the presence of 0.5 grm. to 1 grm. of manganous chloride.

Finally, it appears as the result of an investigation, that the titration of oxalic acid by potassium permanganate in presence of hydrochloric acid is ordinarily attended with some inaccuracy due to liberation of chlorine from the hydrochloric acid; that this tendency may be overcome by the presence of a manganous salt—either the sulphate or chloride; that 1 grm. of the manganous salt is enough to so affect the conditions of equilibrium that titrations in moderate volumes  $(100^{ems})$  and in presence of hydrochloric acid ( $5^{ems}$  to  $15^{ems}$  of the strong acid) may be conducted with safety and reasonable rapidity, either with or without sulphuric acid, at the ordinary atmospheric temperature.

\* Loc. cit.

Ammonium	HCl.	MnCl <sub>2</sub> .	D (II	<b>a a</b>	a a	16 (1)	KMnO4	Error.
oxalate.	strongest	$4H_2().$	BaCl <sub>2</sub> .	$SrCl_2$ .	CaCl <sub>2</sub> .	MgUI <sub>2</sub> .	usea.	om 2
em <sup>o</sup> .	emº.		grams.	grams.	grams.	grams.	ems.	em.
25	Ð	0.9					26.05	0.00
25	5						27.45	+1.40
25	อั		2				26.50	+0.45
25	5			2			26.53	+0.48
25	5				2		26.36	+0.35
25	5					2	26.13	+0.08
25	5	0.5	2				26.05	0.00
25	5	0.5		2			26.10	+0.05
25	5	0.2			2		26.10	+0.05
25	5	0.2				2	26.05	0.00
25	10	1.0.	2				26.10	+ 0.02
25	10	1.0		2			26.05	0.00
25	10	1.0			2		26.06	+0.01
25	10	1.0				2	26.11	+0.06

Volume at beginning of titration =  $140^{\text{cm}3}$ . Temperature =  $20^{\circ}$ - $24^{\circ}$  C.

AM. JOUR. Sci .-- FOURTH SERIES, VOL. VII, NO. 42 .-- JUNE, 1899. 31

# SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. On the Influence of Electric Oscillations on Vapors.-It has been pointed out by KAUFFMAN that when the vapors of various chemical compounds are subjected to the influence of electric oscillatory discharges the results obtained are: (1) the vapor becomes luminous, (2) it is crossed by spark discharges, generally of a green color, or (3) it remains dark, at least until a very high pressure is reached. More than fifty vapors were examined in this way, and the results, while too few to permit of general deductions, yet appear to indicate certain constitutive influences. Thus, for example, the aromatic amines for the most part become luminous and show quite similar appearances, the facility with which luminosity occurs appearing to be partly dependent on the basic character of the amine; since compounds which have lost their basic character by substitution, such as nitraniline and tribromaniline, no longer become luminous by the discharge. Cyclic compounds, however, containing nitrogen, do not appear to follow this rule. In the case of hydrocarbons, aliphatic compounds and the more simple benzene compounds remain dark until a very high pressure is reached, though most of the hydrocarbons containing two or more benzene rings readily become luminous. During luminosity, it was noticed that in all cases the vapor acted as a conductor .-- Zeitschr. phys. Chem., xxvi, 719-727, August, 1898. G. F. B.

2. On the Occlusion of Oxygen and Hydrogen by Platinum black .-- In experiments made by MOND, RAMSAY and SHIELDS to test the occlusion of oxygen and hydrogen in this way, the platinum black was saturated with hydrogen, heated at 184° under reduced pressure, then placed in an ice calorimeter and allowed to reabsorb the gas. It was found that 68.8 calories were evolved for every gram of hydrogen occluded. In the opinion of the authors the argument offered by Berthelot in support of the existence of the compounds Pt<sub>30</sub>H<sub>2</sub> and Pt<sub>30</sub>H<sub>3</sub> are not justified by the facts. Moreover they conclude that the difference between palladium and platinum, in their behavior towards hydrogen, as stated by Favre, is due simply to the presence of oxygen in the platinum black. On attempting to remove the oxygen from platinum black, in order to determine its heat of occlusion, it was noticed that reducing agents, while eliminating the oxygen, were themselves occluded and retained obstinately. It was also observed that hydrogen does not remove all the oxygen, but only replaces that at first removed, both gases being simultaneously occluded. On saturating platinum black with hydrogen and exhausting it at 184°, it was found that, on allowing it to come in contact with small quantities of oxygen, the addition of more oxygen beyond a certain point, caused the pressure to increase.

On adding oxygen, however, up to atmospheric pressure, a further small quantity of the gas was absorbed and the heat simultaneously developed represented the true heat of occlusion of this quantity of oxygen. The results obtained were in close agreement with others obtained indirectly, giving as a mean 11 calories for every gram of oxygen occluded. This value agrees well with that given by Thomsen for the heat of formation of platinous hydroxide. Possibly, therefore, the two phenomena may be identical, the water required being present in platinum black dried in a vacuum.

In a subsequent investigation, the authors studied the action of palladium black in occluding gases. Prepared in the same way as platinum black, it contains 1.65 per cent or 138 times its volume of oxygen. But this oxygen, unlike that in platinum black, cannot be removed by heating to dull redness in a vacuum, but must be heated in a current of hydrogen. When heated in oxygen the palladium black absorbs it, up to a red heat, yielding a brownish black substance, which does not lose its oxygen on heating to redness in a vacuum. Nearly 1000 volumes are absorbed, an amount about three-fourths of that required to form the oxide PdO. Over 1000 volumes of hydrogen are absorbed by palladium black, though only 873 volumes are occluded, the rest having formed water with the oxygen present. About 92 per cent is removed by the air pump at the ordinary temperature, the rest at 444°. The palladium sponge from this experiment occluded 852 volumes of hydrogen, of which 98 per cent was extracted in a vacuum at ordinary temperatures. The heat of occlusion for hydrogen was found to be 46.4 calories for each gram of the gas ; or 43.7 if the work of the atmosphere be allowed for. The heat developed per gram of oxygen occluded, determined indirectly, was found to be 11.2 calories, a value intermediate between that found by Thomsen for the heat of formation of palladious and palladic hydroxides; favoring the idea that this occlusion of oxygen is a true oxidation. The atomic ratio of palladium to hydrogen in the fully charged metal varies between 1.37 and 1.47; agreeing closely with the formula Pd, H, as suggested by Dewar. -Proc. Roy. Soc., 1xii, 50-52, 290-293; J. Chem. Soc., 1xxiv, ii, 599, 600, December, 1898. G. F. B.

3. On certain Derivatives of Acetylene.—It has been observed by ERDMAN and KÖTHNER that when acetylene is passed over finely divided copper heated to  $400^{\circ}-500^{\circ}$  it is decomposed into hydrogen and carbon, the latter appearing in the graphitic condition. At temperatures below  $250^{\circ}$ , however, the copper unites with the gas, forming a yellowish-brown compound which is not explosive. This new substance may be more readily prepared by heating finely divided cuprous oxide in a current of acetylene at  $250^{\circ}$ . It is very bulky, and has the composition  $C_{41}H_{44}Cn_{34}$ . When heated with zinc dust in excess it yields 20 per cent of an oil having an odor like Cancasian naphtha and boiling between  $190^{\circ}$  and  $250^{\circ}$ . Well-defined acetylides of the alkali metals are not easy to prepare. Rubidium, though acted on by acetylene at low temperatures, gives rise to no definite product. Zinc and mercury are scarcely acted on, and iron, like copper, acts catalytically, inducing condensation to oily hydrocarbons. Acetylene produces no precipitate in solutions of thallium, lead, cadmium, iron, nickel, cobalt, platinum, iridium, and rhodium. Gold chloride gives a black precipitate, changing to metallic gold on warming. Palladium chloride gives a brown precipitate soluble in ammonia. Copper acetate yields a brownish-red and silver nitrate a white precipitate. By saturating a hot solution of mercuric nitrate with acetylene, mercurocarbide nitrate HgC : CHg. HgNO<sub>3</sub>, H<sub>2</sub>O separates in small white crystals. It yields acetaldehyde on treatment with dilute acids.—Zeitschr. anorg. Chem., xviii, 48-58, 1898.

G. F. B.

4. On Eutropic Series of the Calcium Group.—In 1896 Linck proposed the term catameric eutropy or more briefly eutropy, for those special cases of isomorphism in which the geometrical and physical characters of members of a series increase or decrease regularly with increase of the atomic mass of the varying element; as is the case for example in the potassium, rubidium and cæsium compounds described by Tutton. Subsequently he called attention to the fact that the quotients obtained by dividing the crystal volumes of the different members of such a series by their molecular volumes are in the ratio of simple natural numbers.

These relations have been recently tested by EPPLER, who finds that they both hold good in the calcium-barium-strontium group, with one or two exceptions, as in the case of the three anhydrous sulphates, anhydrite, celestite and barite. In his paper he has brought together and compared numerous data concerning the crystallized compounds of this series of elements, giving new geometrical, optical and density determinations. In the case of cubic crystals the volume is unity and the above mentioned quotient is inversely proportional to the molecular volume. In the cubic oxides, fluorides, chlorides and nitrates of calcium, strontium and barium, the ratios are 11:15:19, 14:17:20, 18:19:20, and 20:21:22 respectively; thus decreasing with the increase in molecular mass. Although lead compounds are frequently isomorphous with those of calcium, strontium and barium, they do not belong to the same eutropic series, the physical constants falling between those of calcium and strontium or before or after those of the barium salt corresponding.-Zeitschr. Kryst. Min., xxx, 118-175; J. Chem. Soc., lxxiv, 560, December, 1898.

G. F. B.

5. The distribution of Vanadium.—It was shown by HASSELBERG in 1897 (Astrophys. Jour., vi), that the mineral rutile contains vanadium in small but varying amount. He has now (ibid., ix, 143) continued his investigation to a considerable number of meteoric stones, and concludes from this that vanadium is always present in them, although it has not been detected in meteoric irons. A recent paper by Hillebrand (this Journal, vi, 209) has

shown that both vanadium and molybdenum are widely distributed in rocks, the former probably present in the silicates of the amphibole or pyroxene group and in the biotites.

6. Determination of time of vibration of very high notes.— F. MELDE reviews the various methods that have been suggested and used for such determinations and divides them into two groups: A, the subjective; B, the objective. Under A fall the determinations carried out by the human ear, such as the comparison of sounds, one of which is used as a standard. Determinations of notes of 6144 vibrations have been made by this method; for higher notes the method becomes inapplicable. To the subjective method also belongs the difference-tone method, which consists in measuring a third tone by the use of two primary tones. Notes of 8692 vibrations have thus been measured. To the objective method belong the various graphical and photographic methods. In conclusion the author points out the applicability of sensitive flames for the measurement of high notes.— *Wied. Ann.*, No. 4, 1899, pp. 781-793. J. T.

7. Heat conductivity of different kinds of glass.—A great number of determinations have been made by Focke and by Paalhorn of the thermal conductivity of glass which differ greatly in value. A. WINKELMANN endeavors to reconcile the results and concludes that it cannot be decided which determinations are the better. The discrepancies are in part due to the different ranges of temperature employed. The author concludes that it is desirable to investigate further the dependence of the conductivity of glass upon temperature.— Wied. Ann., No. 4, 1899, pp. 794-802.

8. Absorption of Electric Waves by different substances.—The recent experiments in wireless telegraphy have excited interest in the question of the electrical opacity of non-metallic substances. E. BRANLY and G. LEBON have undertaken a research upon this question. A coherer together with a battery and a bell were placed in a cavity in the substance which was to be investigated. The substances employed were stones, blocks of cement, and boxes of sand. The electric waves were excited by a Rhigi oscillator placed outside the substance. It was found that the opacity depends upon the nature of the substance. The transparency is very great in the case of sand and the kind of building stone employed. It was extremely feeble with Portland cement. The opacity increases with the thickness. Humidity clearly increases the opacity.—*Comptes Rendus*, April 14, 1899, pp. 879-882.

J. T.

9. Radiations of Uranium.—H. BECQUEREL concludes further study of these radiations by the following conclusions: The radiation of radio-active bodies approaches approximately in character to X-rays more nearly than to ordinary light. The most singular fact connected with these radiations is the spontaneous emission of such radiations without known cause. If it could be shown that this radiation occurs without the consumption of energy, one could compare the state of uranium to that of a magnet. We can also compare the state of uranium to that of phosphorescent bodies which seem to conserve their state of phosphorescence indefinitely. The photographic and phosphorescent effect, however, of the uranium radiation indicates a consumption of energy. This consumption is extremely feeble, and seems to indicate that uranium can emit its unknown radiation for a long period of years apparently without sensible diminution.—*Comptes Rendus*, March 27, 1899, pp. 771–776. J. T.

10. Source of Uranium Radiations.—Prof. W. CROOKES suggests that uranium, thorium, polonium and radium have the power of separating rapidly moving molecules from slowly moving ones and appropriating a portion of the energy of the former. This energy may be used in dissociation and maintaining radiations in the ether. The air in the neighborhood of such substances would be cooled. This cooling is so small as to escape detection, and therefore the energy appears to be created out of nothing. The author computes that air contained in a room  $4 \times 8 \times 7m$ . could supply one h.p. for fifteen hours.—Comptes Rendus, 128, pp. 176–178, 1899.

11. Phosphorescence at low Temperatures.—A. and L. LUMIÈRE have found that the phosphorescence of calcium and zinc sulphides produced by exposure to an arc light disappears wholly at about  $-50^{\circ}$  C. When exposed to a magnesium light it disappeared between  $-70^{\circ}$  and  $-90^{\circ}$ . When the exposure to a magnesium light is made at  $-191^{\circ}$  C. the temperature of liquid air and the body is heated, phosphorescence begins to appear at  $-180^{\circ}$  C. and increases with the heating. Röntgen rays act like ordinary light.— *Comptes Rendus*, 129, pp. 549-552, 1899. J. T.

12. Recueil Données numériques publié par la Société Française de Physique. Optique par H. DUFET. Deuxième fascicule. Propriétés optiques des solides; pp. 417-785, Paris, 1899 (Gauthier-Villars) .-- This volume contains tables of physical constants in the department of optics, prepared under the direction of the Physical Society of France. The opening tables give the refractive indices for different wave-lengths of certain remarkable substances, as calcite, quartz, fluorite, halite, and so on. Then follows a table of refractive indices for certain important samples of glass. After this we have an alphabetical list of inorganic solids, largely mineral species, with their optical properties arranged in tabular form; references are given to the original publication where the facts were given. This portion covers pages 466 to 632. A like table for organic solids follows, and then other tables giving the influence of temperature on optical properties, and allied subjects, close the volume. This enumeration of its contents will show how much this valuable book of reference contains.

# II. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Icthyologia Ohiensis by C. S. Rafinesque, a verbatim reprint; by R. E. CALL. Svo, 175 pp. Cleveland, 1899. (The Burrows Brothers Co.)-Rafinesque's genera and species, whether based on actually existing forms or Audubon's cruel jokes, or in later life evolved from his own diseased mind, have been a stumbling block to the systematic zoologist for more than half a century. The extreme rarity of many of his published works has increased the difficulty of recognizing the forms he described and has doubtless often forced subsequent authors to ignore him unwillingly. The late G. W. Tryon many years ago republished Rafinesque's conchological works, and now Dr. Call and his publishers give us the work on American fishes in this handsome volume, issued in a limited edition of 250 numbered copies. The volume contains a brief biographical sketch of Rafinesque, an account of his ichthyological work, a verbatim reprint of the Ichthyologica Ohiensis (of which only eight copies are now known to exist), a bibliography of his papers on fishes, and a reproduction of a previously unpublished letter from Rafinesque to Dr. Daniel Drake of Cincinnati, containing a sketch of one of the fishes described. It seems ungrateful to criticise a work of this kind for its omissions, but a general index is much needed, the reprint of the original index of the Icthvologica with references to the genera and English names being almost useless for reference.

If the "excentric naturalist" could have foreseen the appearance, before the end of the century, of this luxurious volume devoted to a reprint of the work to which he gave himself with such prodigality of unrewarded zeal, he might have forgiven and forgotten the neglect and scorn of his cotemporaries and retained his reason through the unhappy later years of his life. S. I. S.

2. Elementary Physiology; by BENJAMIN MOORE, M.A. pp. 295. New York, 1899. (Longmans, Green & Co.)—This elementary text-book differs in several respects from many other books of its class. First, a relatively large portion of the text is devoted to the description of the structure of the animal body. Since the functions of the organism are so closely connected with its morphological characters, a somewhat comprehensive survey of the latter becomes highly essential to a well-conducted course in physiology for beginners. The usefulness of the present textbook is greatly increased by an unusually large number of wellselected illustrations. Second, in the consideration of the various departments of physiology due appreciation of the relative importance of the phenomena discussed has usually been shown. Too many of the elementary text-books are unsatisfactory in this respect: they either unduly emphasize certain actions of the body, or omit entirely chapters which do not permit of easy treatment. Professor Moore's little book certainly does not err in the latter respect, and it may even be questioned whether occasional topics

have not been introduced with too great detail for the beginner. Third, the reader is not allowed to forget that physiology is an experimental science and should properly be taught as such; accordingly, the general method of the book tends to encourage observation and experiment. A series of carefully defined exercises forms a useful appendix.

3. Experimental Morphology, Part II; by C. B. DAVENPORT. New York, 1899 .- In this second installment of his valuable treatise Dr. Davenport considers the effects of chemical and physical agents on growth. Plants lend themselves so readily to observations respecting growth, that they have received from Dr. Davenport a degree of attention in this work which compels the student of plant physiology to accept his aid. The literature of the whole province has been carefully examined, and few omissions can be noted in the references. On the whole, the editorial work has been wonderfully well done, and the errors are so few that they need not be mentioned here; they do not appear likely to mislead seriously any students who make use of the vast amount of material which has been gathered patiently, and for the most part has been well arranged. The botanical phases of experimental morphology are at present attracting a large number of enthusiastic students who are moved to consider questions in a broad way, and are stimulated by just such books as Dr. Davenport's, to ask some of these questions, at first hand, of nature. G. L. G.

4. Recherche, Captage et Aménagement des Sources Thermo-Minérales. Origine des eaux Thermo-Minérales; Géologie; Propriétés physiques et chimiques. By L. DE LAUNAY, pp. x, 635, large 8vo. Paris, 1899 (Librairie Polytechnique Baudry et Cie., éditeurs) .-- M. De Launay has added another to the series of highly valuable practical works prepared by him. The previous volumes on Mineral Deposits, on the Gold Mines of Transvaal, and the Diamonds of South Africa, have been noticed in earlier numbers of this Journal. The present volume discusses thermal springs in different parts of the world. The treatment is thorough and exhaustive. The origin of the springs and their relation to geological and topographical features is first taken up. Then comes a discussion of their chemical composition with the salts and gas in solution, accompanied by numerous analytical tables. Following these are data in regard to the temperature at different springs, ranging, for example, from 81°5 at Chaudes-Aigues (Cantal) to 27° at Uriage (Isère). The latter half of the work goes more minutely into the account of the individual localities in different parts of the world, giving a large amount of very interesting information about a multitude of places. The work closes with details in regard to the distribution of the hot water to the different establishments, with numerous excellent illustrations.

#### OBITUARY.

Dr. FRANZ RITTER VON HAUER, the distinguished Austrian geologist, died March 20th, at the age of seventy-seven years.

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Plate II.



CYCADEOIDEA INGENS, Ward (type).



Plate III.



CYCADEOIDEA INGENS; type specimen. Longitudinal section through male flower.





CYCADEOIDEA INGENS; transverse sections through male flower.



Plate V.

![](_page_530_Picture_2.jpeg)

![](_page_531_Picture_0.jpeg)

![](_page_532_Picture_0.jpeg)

![](_page_533_Picture_0.jpeg)

Am. Jour. Sci , Vol. VII, 1899.

![](_page_534_Figure_1.jpeg)

Plate VI.

![](_page_535_Picture_0.jpeg)

![](_page_536_Figure_0.jpeg)

CYCADEOIDEA INGENS, Ward (type); leaf structure

![](_page_537_Picture_0.jpeg)

![](_page_538_Figure_2.jpeg)

![](_page_538_Picture_3.jpeg)

![](_page_539_Picture_0.jpeg)










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